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AN XPS EXAMINATION OF THREE PYRITE POWDERS

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Samples submitted for analysis by Dr. G. Jean

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ABSTRACT

The surface composition and surface chemistry of three pyrite ore powders, submitted by the "Separation and Characterization Section" of HPRL were determined by X-ray photoelectron spectroscopy (XPS).

RÉSUMÉ

La surface de trois minerais du pyrite, provenant de la section "Séparation et caractérisation", a été analysée par la spectroscopie photoélectronique à rayon-X (XPS).

AN XPS EXAMINATION OF THREE PYRITE POWDERS

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EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

A. SAMPLE PREPARATION

After drying at 100°C in an oven overnight, each specimen was placed on an Al foil substrate (15 mm x 10 mm) using double-sided 3M brand sticky tape. Enough powder was used to entirely cover the tape to a depth where it was obscured (several mm's). The Al foil strip was then attached to the sample holder. This holder was then mounted on the specimen insert probe and evacuated to $\approx 10^{-6}$ torr in the preparation/pumpdown chamber.

B. INSTRUMENTATION

A combination x-ray photoelectron (XPS) and Auger electron spectrometer (AES) manufactured by Physical Electronics Division, Perkin-Elmer Corporation (PHI-548E) having depth profiling capability (Ar^+ 5KeV ion gun Model PHI-4303), specimen introduction and transfer fore-chamber (PHI-2100) and multiple-technique analytical computer system (MACS) was employed for this investigation. The base pressure of this instrument is $\approx 2 \times 10^{-10}$ torr (ultra-high vacuum, UHV).

X-ray photoelectron spectroscopy (XPS) also called electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) are highly surface sensitive, direct and in many cases non-destructive. Both XPS and AES readily provide qualitative information (which elements are present), by probing the outermost 1-5 nm region of a sample's surface. When calibration techniques (element and instrument sensitivity factors) are used, semi-quantitative and in some cases quantitative surface composition data is possible.

All elements, except hydrogen and helium can be detected with an ultimate sensitivity approaching 10^{-9} gm cm^{-2} of surface. Usually it is possible to confirm chemical environment (oxidation state, co-ordination number) of a surface sited element from XPS binding energies (chemical shift information).

Extensive reviews of XPS (1-5) theory and use are available. Details of the specifications and features of the PHI multi-technique XPS/AES instrument utilized in this study are available (6).

Each sample was placed on an introduction sample holder, mounted on the specimen insert probe and evacuated to ≈ 10^{-7} torr in the preparation fore-chamber. XPS analyses were performed at ≈ 10^{-9} torr in the analytical chamber using a dual Al/Mg anode equipped x-ray gun operating at 300 W (15 KeV x 20 mA) in the Mg kα mode. The resulting x-rays of energy ≈ 1254 eV were directed onto an ≈ 5 mm^2 area of the sample.

The quantity of electrons photoejected by x-rays (XPS) and their kinetic energies are monitored using a high resolution double pass cylindrical mirror electron energy analyzer (CMA) with a coaxially mounted electron gun and associated electronics. The entire analytical operation is computer controlled. A spectrum of peak intensity (electron counts) vs. energy (binding energy in XPS, kinetic energy in AES) is then plotted. Samples are normally examined using two XPS (AES) scanning modes:

(a) initial "surveying" for determining all elements present; and

(b) "multiplexing" specific regions of the survey at greater resolution for quantitative and/or chemical structure information

The XPS "survey technique" can identify elements present down to the minor element level by sweeping the binding energy scale (0 → 1254 eV) in 1 eV/100 microsecond increments using a CMA pass energy of 100 eV. Spectrum acquisition times for acceptable S/N level spectra is usually 15 minutes. For the "multiplex technique", ultimate resolution is achieved at lower pass energies, typically 25 or 50 eV and binding energy windows of either 10, 20 or 40 eV depending on the complexity of an individual photoelectron line envelope and on the proximity of one peak to another. Acquisition times for multiplex spectra vary greatly depending on the element's surface concentration. The time required to give an acceptable S/N multiplex spectrum for elements present at the major and minor level are typically 5 minutes and 15 minutes respectively.

The carbon (C 1s) signal is used to determine the degree of specimen charging; an electron flood gun (specimen neutralizer) is used to greatly reduce charging of insulators and hence eliminate identification problems caused by differential charging (ghost) peaks. Thus all XPS photoelectron lines are referenced to the accepted hydrocarbon C 1s binding energy of 284.6 eV. Gold foil is used to calibrate the energy scale of the spectrometer (Au $4f_{7/2}$ = 83.8 eV).

DISCUSSION

XPS RESULTS

An XPS surface composition analysis for each of the three powder samples can be found in Tables 1, 2 and 3. Figures 1, 13, and 23 are the XPS survey spectra. Figure 31 is an XPS survey spectrum of the double-sided sticky tape on the sample probe tip.

A. Pyrite #1 (Brown)

The Cl 2p peak position (Figure 5) indicates an inorganic chloride species present in this sample. A small amount of the total Si measured may represent constituents in the double-sided sticky tape used to hold the sample on the probe tip, however the majority of the Si is in the form of an Al-silicate (Figure 7). Note the low C/Si intensity ratio (Figure 1, C/Si = 2.5) compared to that of the sticky tape alone (Figure 31, C/Si = 19). The Fe 2p peak position (Figure 4) indicates the presence of FeOOH and/or Fe_3O_4 type mixed iron oxides. No FeS_2 was observed. The S 2p peak positions (Figure 6) indicate ≈ 60% S^{6+} (sulphate), and ≈ 40% S^{2-} (sulphide).

The Al 2p binding energy is indicative of an Al-silicate (Figure 8) which further substantiates the aforementioned Si interpretation. Trace concentrations of Cr (from $CrCl_3$ or $Cr(NH_3)_6Cl_3$ compounds (Figure 9), Mg and/or K were detected (Figure 10). The Ca 2p peak positions (Figure 11) indicate the presence of ≈ 75% $CaCl_2$ and ≈ 25% $CaSO_4$ or $CaCO_3$. The N 1s peak positions (Figure 12) are characteristic of an NH_3 type species with a trace of an NH_2 species. The increase in the C content from the Blank #3 sample (Figures 3 and 25) indicates the presence of an organic species. The O 1s peak position indicates most of the oxygen present in this sample is sited with the Al and Si as silicate minerals (Figure 2).

B. Powder #2 (Grey)

The Th 4f peak position (Figure 22) does not characterize Th metal, oxide or chloride. It may represent $Th(NO_3)_4 \cdot 5H_2O$, or $Th(Urea)_8Cl_4$, or $Th_3(PO_4)_4$. The Al and Si 2p peak positions (Figures 19 and 20) identify Al-silicates with a small % of Si, possibly attributed to the double-sided sticky tape. The O 1s peak position and intensity (Figure 14) also indicates that the oxygen present in this sample is predominantly sited with the Al and Si as silicate minerals.

The presence of Ca was not detected in this sample. The Cl 2p peak position (Figure 17) is characteristic of a Cl inorganic species. The Fe 2p peak position (Figure 16) denotes the presence of FeOOH, mixed iron oxides, and possibly a trace of FeS. The Cr 2p peak position (Figure 21) is characteristic of any one of four possible compounds: a) CrO_4^{2-}, b) $Cr(Urea)_6Cl_3$, c) $Cr(C_2O_4)_2^{2-}$ or d) $Cr(NH_3)_6Cl_3$. The S content measured (Figure 18) was present in trace amounts, and the S 2p peak position was indicative of a S^{6+} species. An increase in the C content compared to the Blank #3 sample (Figures 15,25) suggests the presence of an organic species.

C. Powder #3 (Blank)

The Si and Al 2p peak positions (Figure 28,29) finger print the presence of Al-silicates with a small % of Si possibly attributed to the double-sided sticky tape. The O 1s envelope is composed of 2 peaks (Figure 24), their positions and intensities indicating a composition of ≈ 60% OH and ≈ 40% (Si-O). The Fe 2p peak position (Figure 26) suggests FeOOH; iron oxides nor FeS_2 are detected. The K content (Figure 30) is quite probably a constituent of the Al-silicates mineral phase present. S is found in trace amounts only, and as deduced from the S 2p peak position (Figure 27) is in the sulphate state.

SUMMARY

Sample #1 (brown powder) shows the largest S content (1.6 wt%), N content (1.1 wt%), Ca content (3.5 wt%) and the largest Cℓ content (13.0 wt%).

Sample #2 (grey powder) shows the largest Cr content (4.3 wt%). It is the only sample in which the presence of Th is observed (2.4 wt%), and it also shows a large content of Cℓ (1.8 wt%).

Sample #3 (blank powder) contains the lowest C composition (12.8 wt%) and the largest Fe (7.2 wt%), Si (24.3 wt%), Al (9.0 wt%), and K (4.2 wt%) concentrations.

REFERENCES

1. Carlson, T.A. Photoelectron and Auger Spectroscopy, Plenum, New York, N.Y.; 1975.

2. Brundle, C.R. and Baker, A.D. (editors) Electron Spectroscopy: Theory, Techniques and Applications, Vol. 1, 2, 3; Academic Press, New York, N.Y.; 1979.

3. Windawi, H. and Ho, F.F.L. Applied Electron Spectroscopy for Chemical Analysis; Vol. 63, in "Chemical Analysis", Elving, P.J. and Winefordner, J.D. (editors); Wiley-Interscience, New York, N.Y.; 1982.

4. Hercules, D.M. Electron Spectroscopy, Analytical Chemistry, 42, 20A-40A; 1976.

5. Bancroft, G.M., Brown, J.R. and Fyfe, W.S. Advances In, and Applications of, X-Ray Photoelectron Spectroscopy (ESCA) in Mineralogy and Geochemistry, Chemical Geology, 25, 227-243; 1979.

6. Palmberg, P.W. A Combined ESCA and Auger Spectrometer, J. Vac. Sci. Technol., 12, 379-384; 1975.

TABLE I

XPS SURFACE COMPOSITION ANALYSIS OF FES_2 POWDER #1 (BROWN)

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Si	11.2	16.2		Al-silicates.
Al	6.0	8.3		
Fe	1.5	4.3		- FeOOH and Fe_3O_4
Ca	1.7	3.5		- 75% CaCl, 25% $CaSO_4$ or $CaCO_3$.
K	0.7	1.4		- trace amounts only.
S	1.0	1.6		- 60% Sulphate, 40% sulphide.
C	37.3	23.1		- Organic C species
O	31.2	25.7		- mostly present as silicate minerals.
Cr	0.6	1.6		- $CrCl_3$ or $Cr(NH_3)_6Cl_3$
Cl	7.2	13.0		- inorganic compound.
N	1.5	1.1		- mostly NH_3, trace of NH_2

TABLE 2

XPS SURFACE COMPOSITION ANALYSIS OF FES_2 POWDER #2 (GREY)

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Si	10.5	15.0		
Al	6.2	8.6		Al-silicates.
Fe	1.6	4.6		- FeOOH, mixed iron oxides and trace FeS present.
S	Trace	Trace		- trace amounts of sulphate.
C	32.3	19.9		- Presence of Organic species.
O	40.9	33.5		- mostly present as silicate minerals
Th	0.2	2.4		
Cr	1.6	4.3		- CrO_4^{2-}, $Cr(Urea)_6\ Cl_3$, $Cr(C_2O_4)_2^{2-}$, or $Cr(NH_3)_6\ Cl_3$
Cl	6.6	11.8		- Inorganic Cl species.

TABLE 3

XPS SURFACE COMPOSITION ANALYSIS OF FeS_2 POWDER #3 (BLANK)

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Si	16.9	24.3		
Al	6.5	9.0		Al-silicates.
Fe	2.5	7.2		- FeOOH only
K	2.1	4.2		- K probably sited in the silicate matrix.
S	0.8	1.3		- trace amounts of sulphate only.
C	20.8	12.8		- Low C present.
O	50.3	41.2		- 60% OH, 40% (Si-O)
Pb	Trace	Trace		

Figure #1

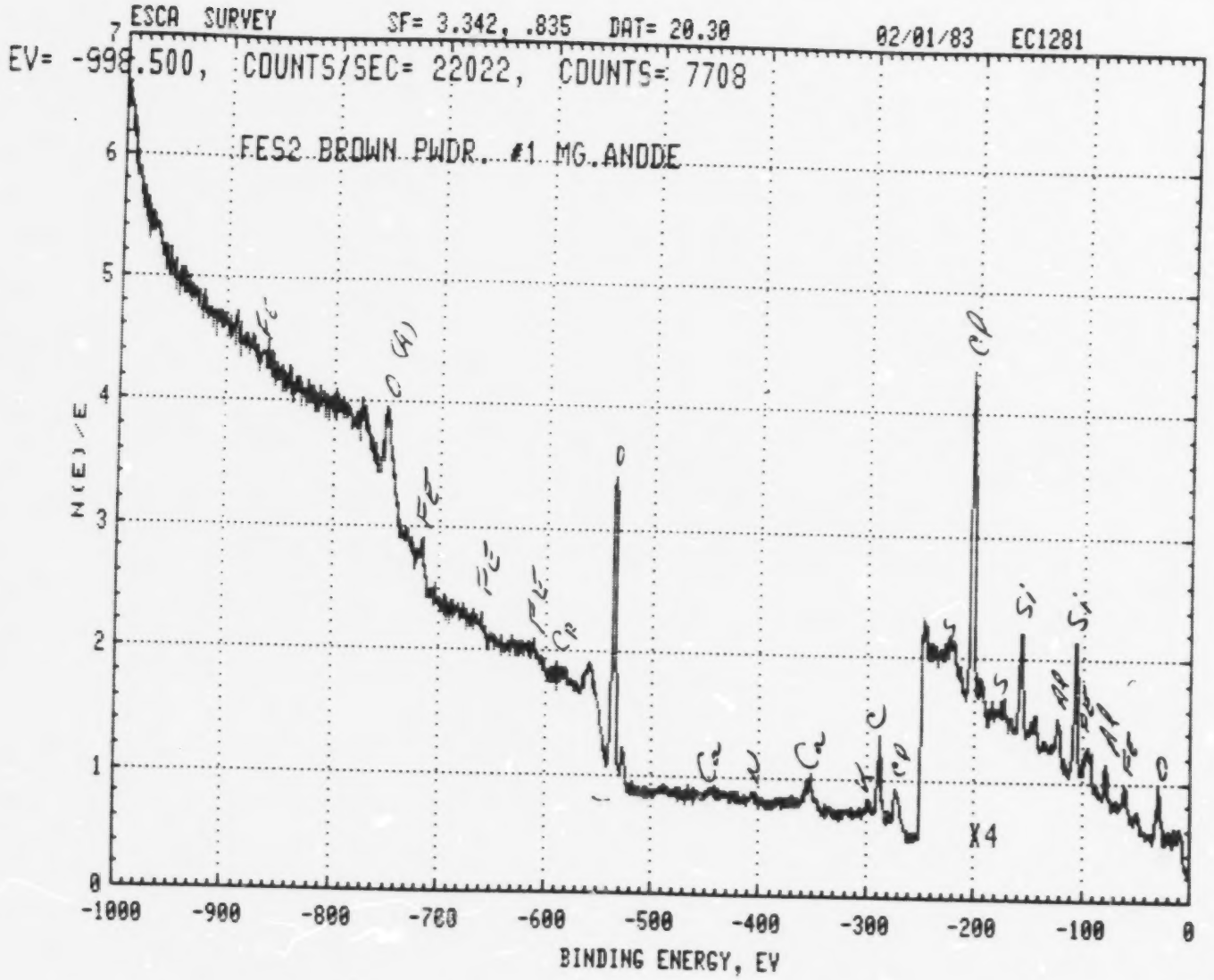

Figure #1

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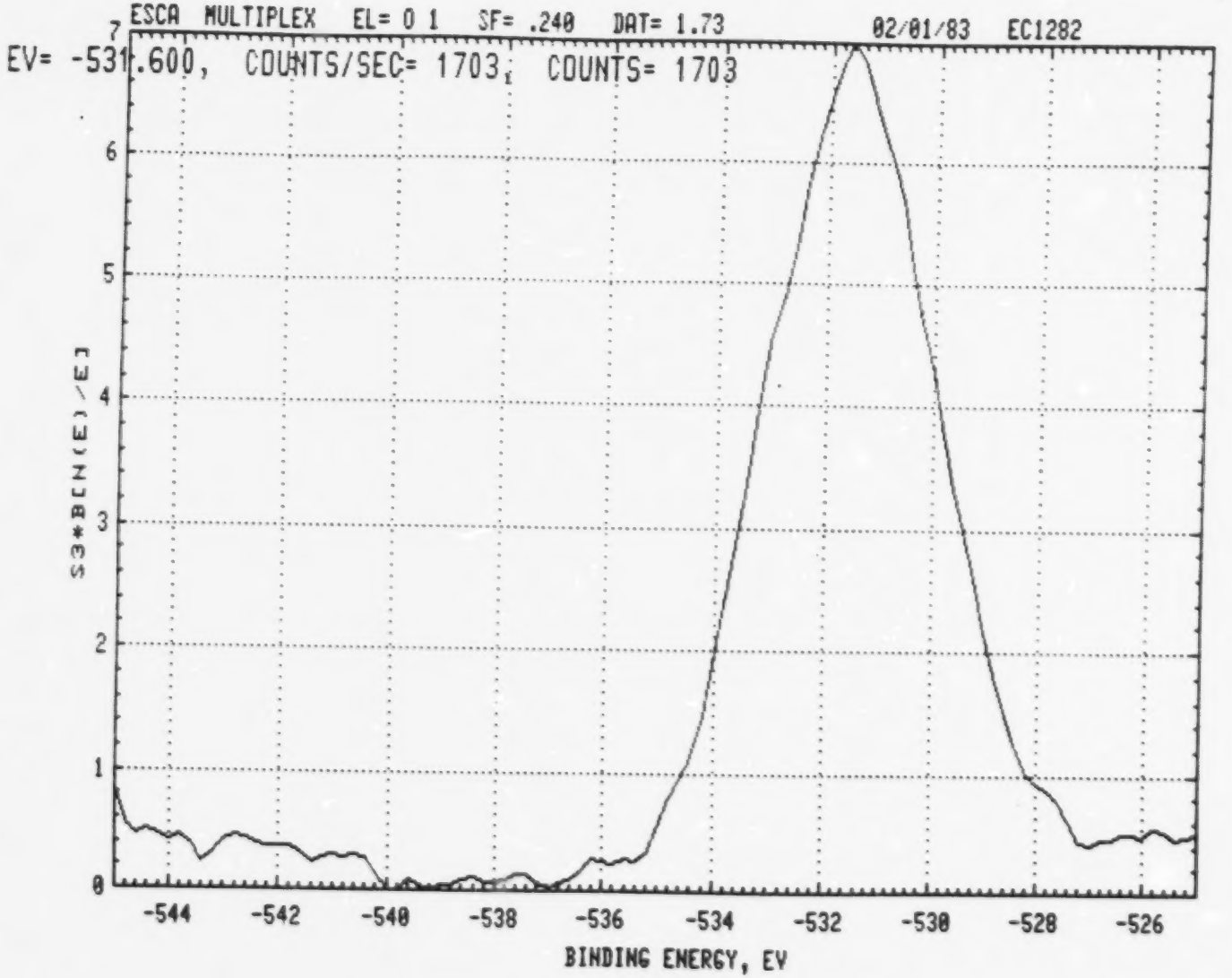

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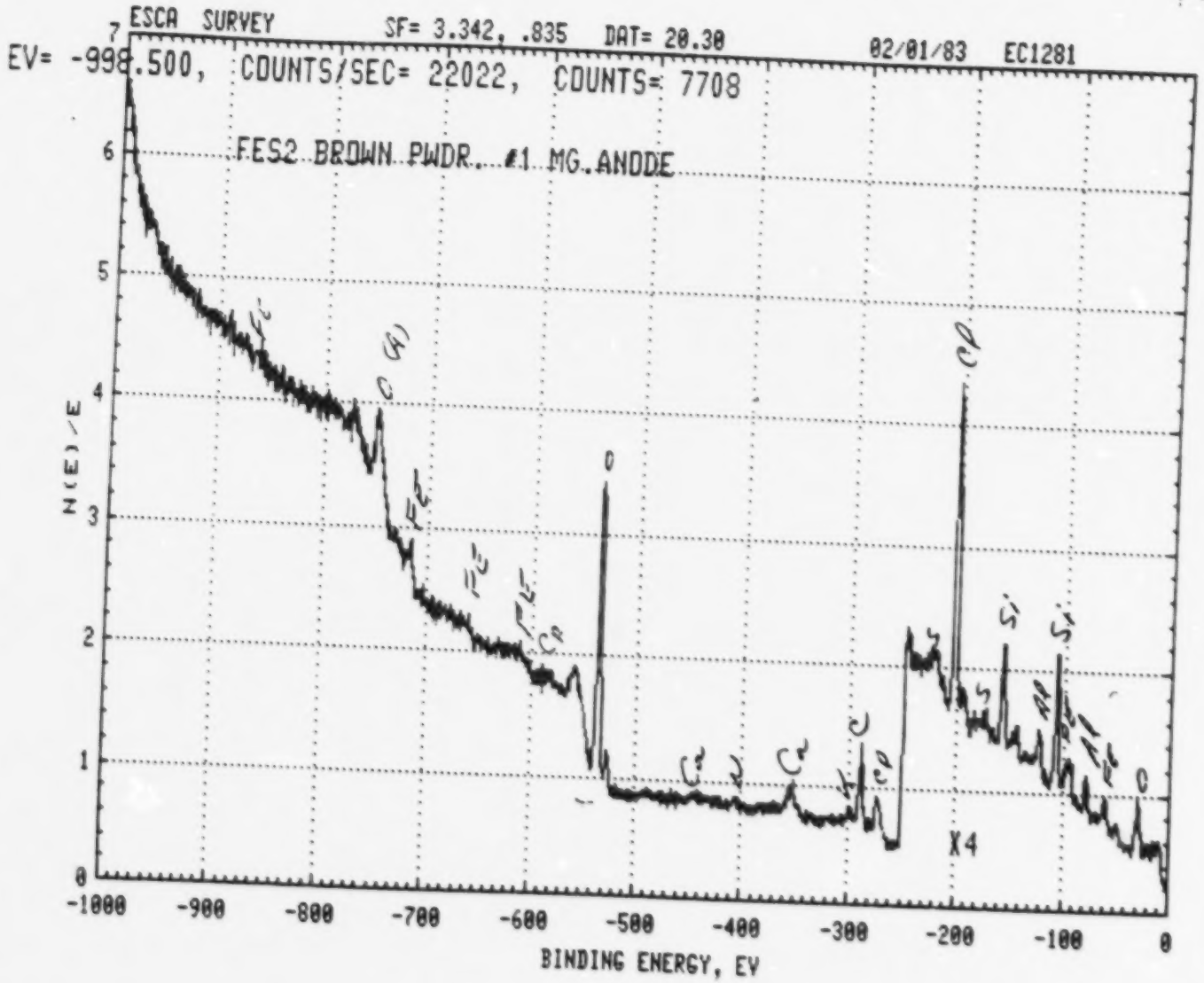
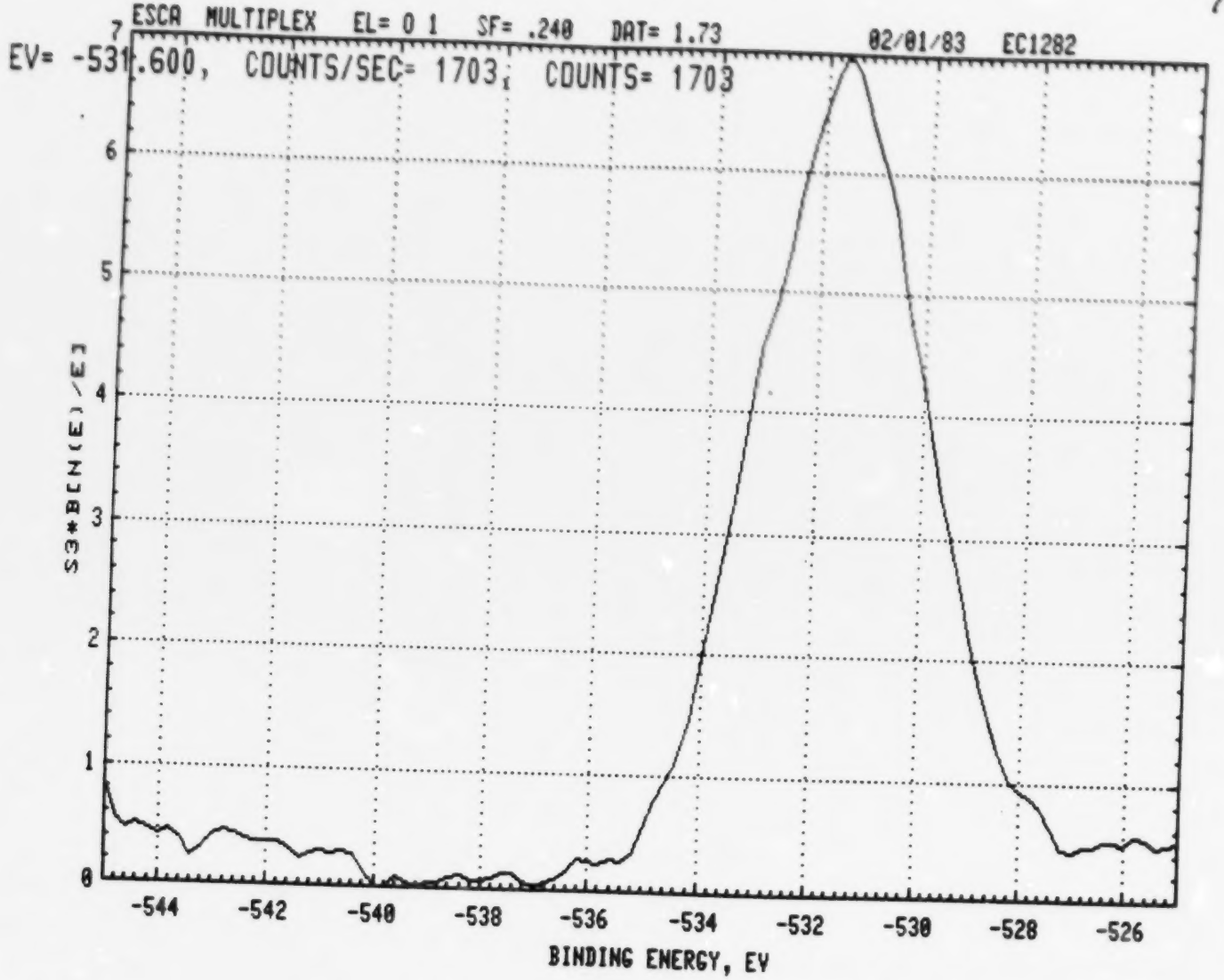


$\frac{23}{4} = 6$

$\frac{5}{6}$

Figure #1

Figure #2.



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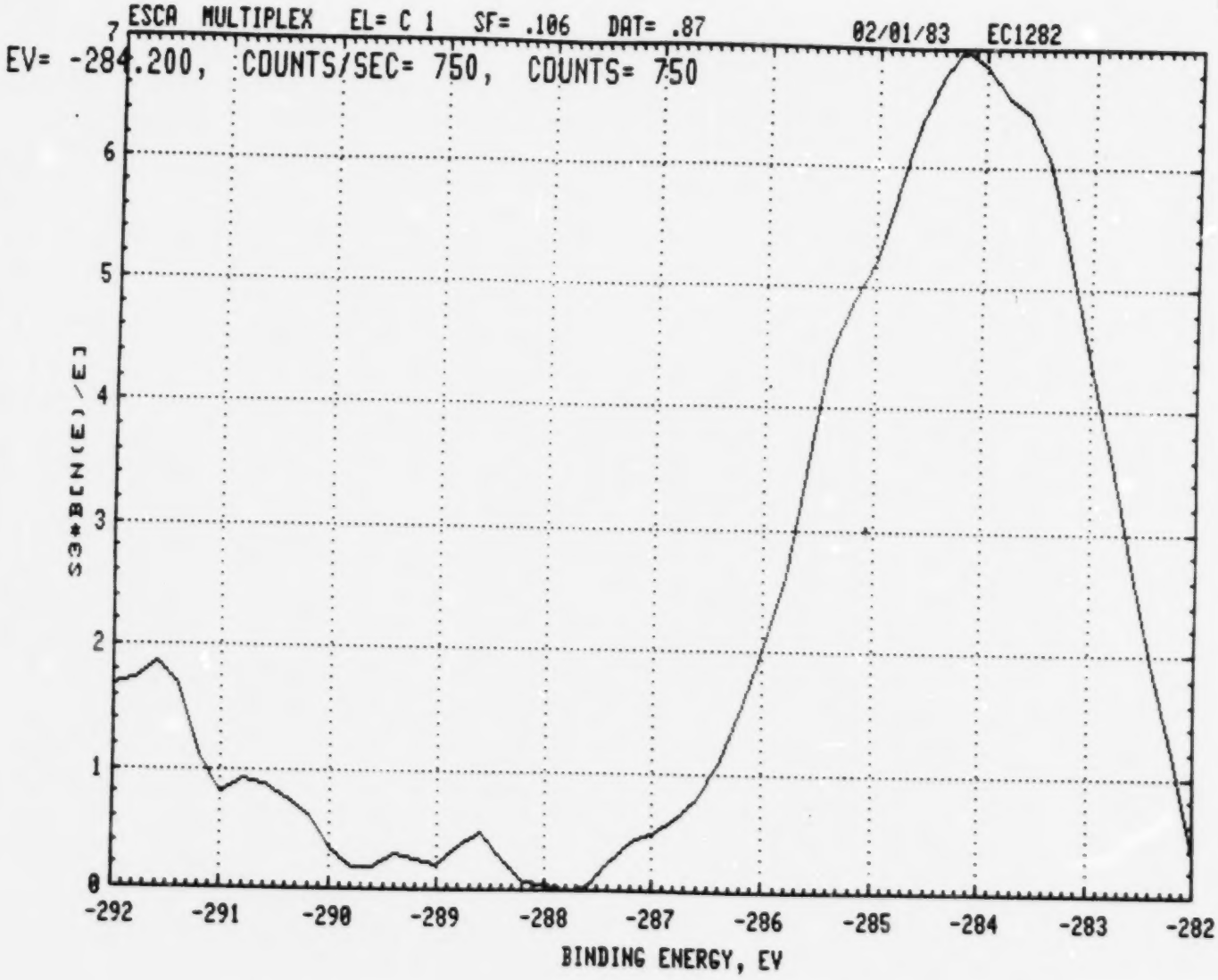

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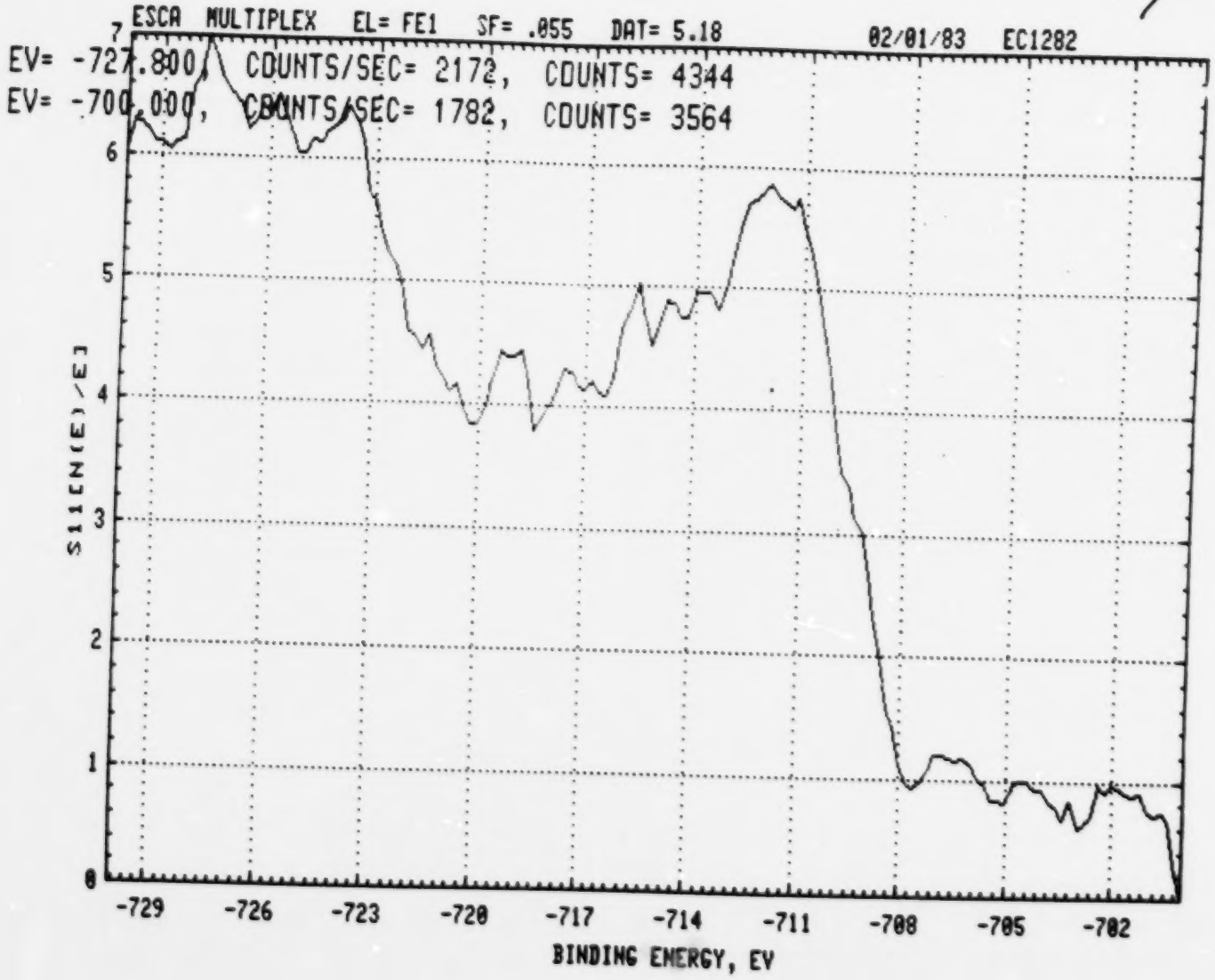

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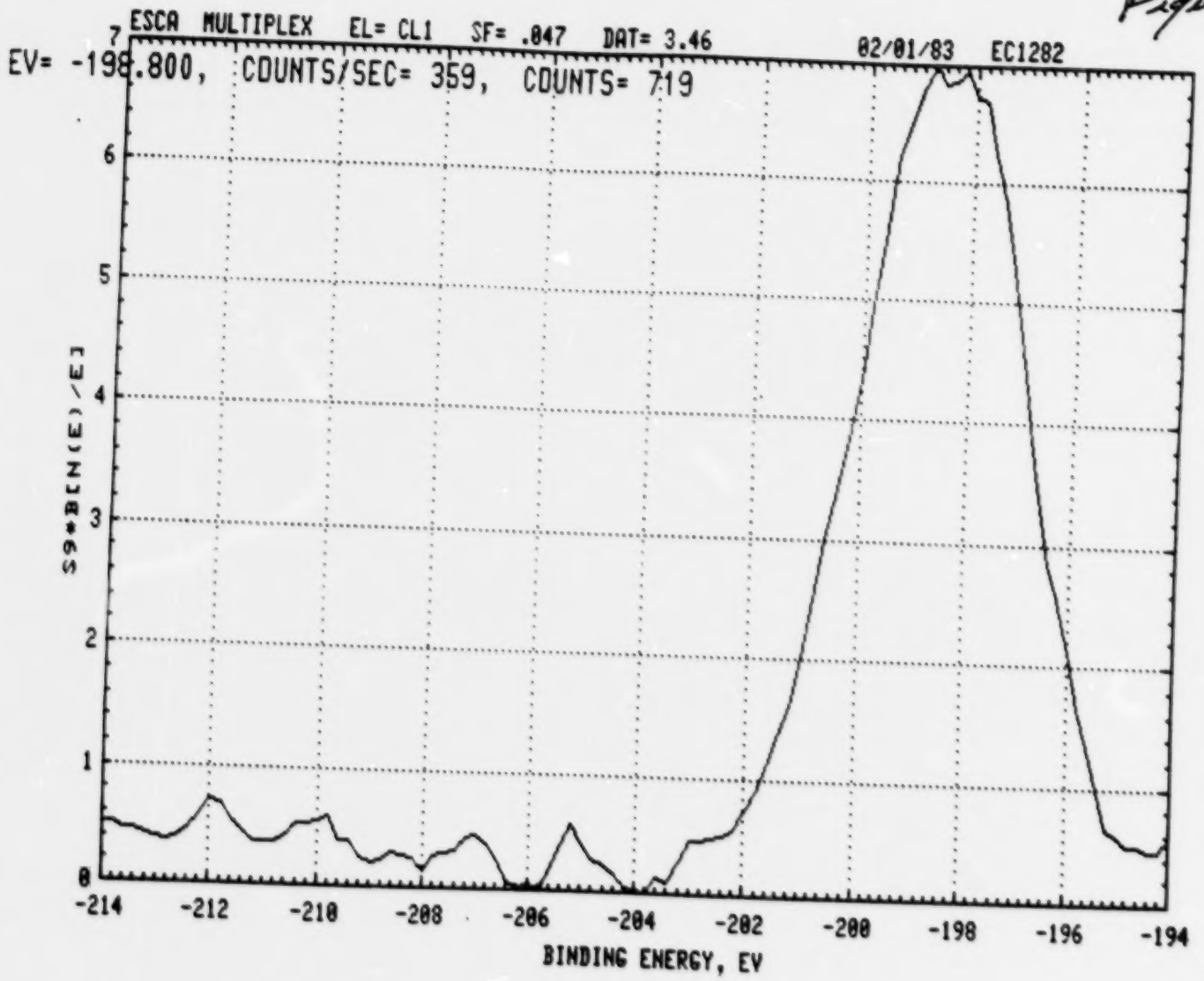

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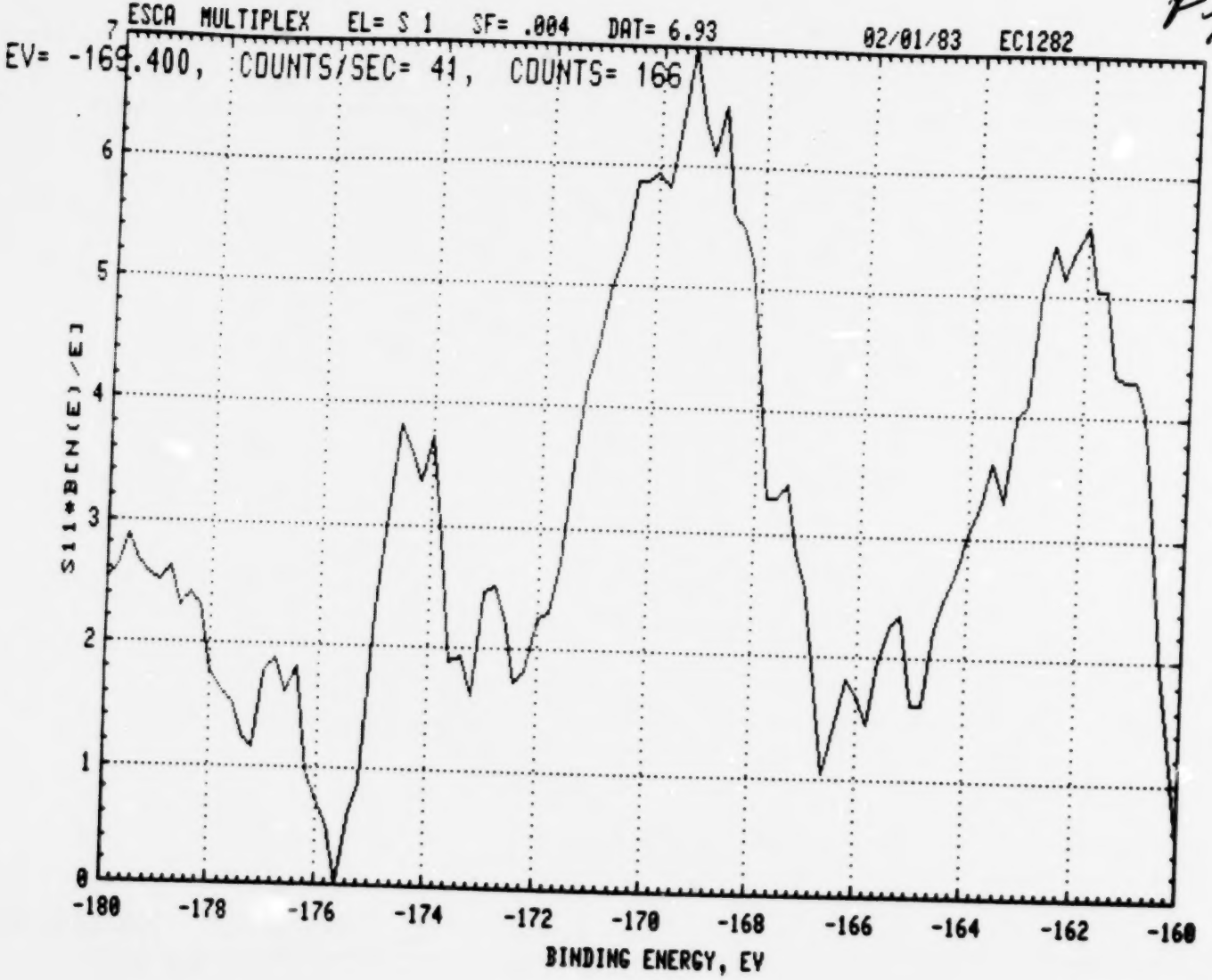

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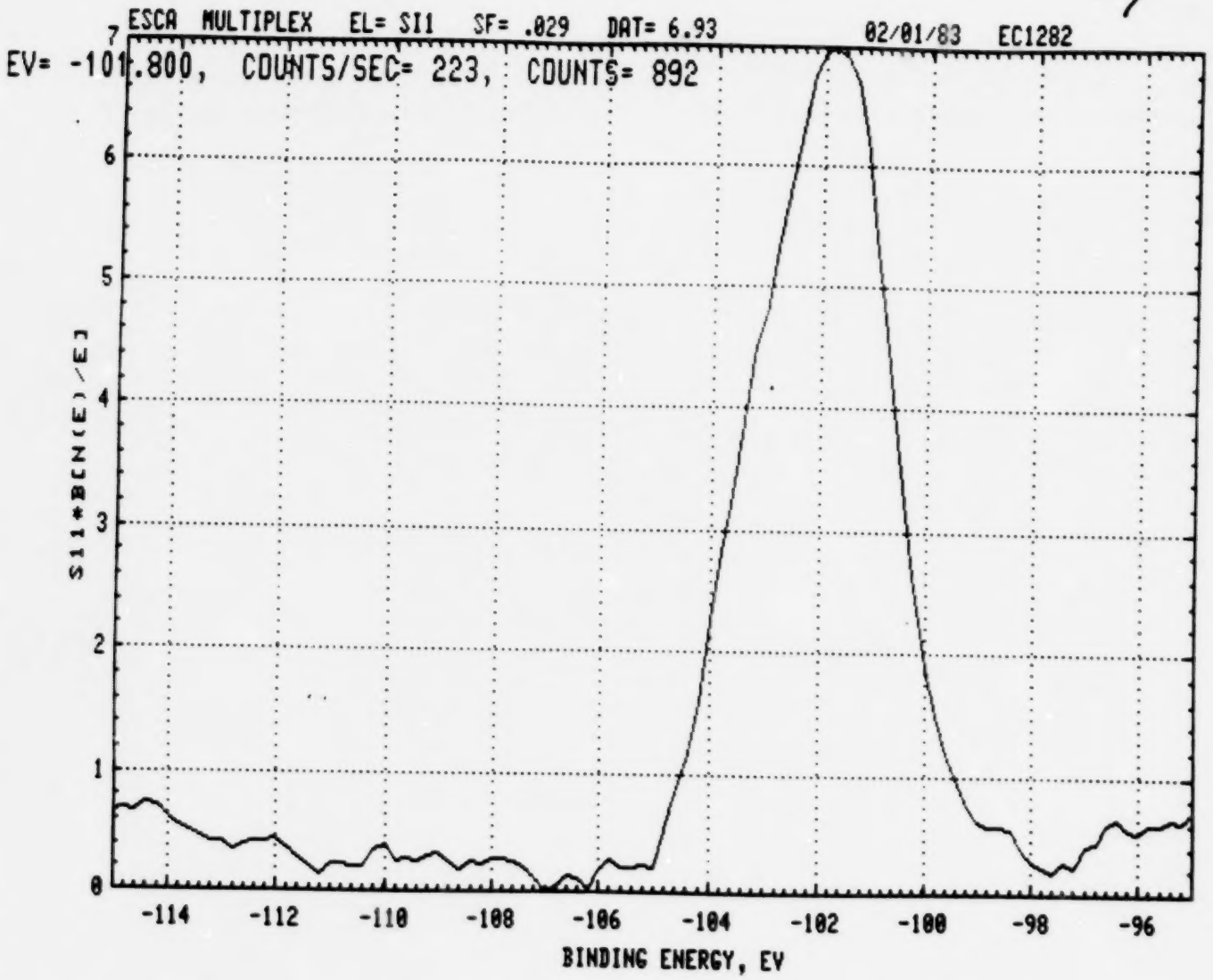
Figure #7



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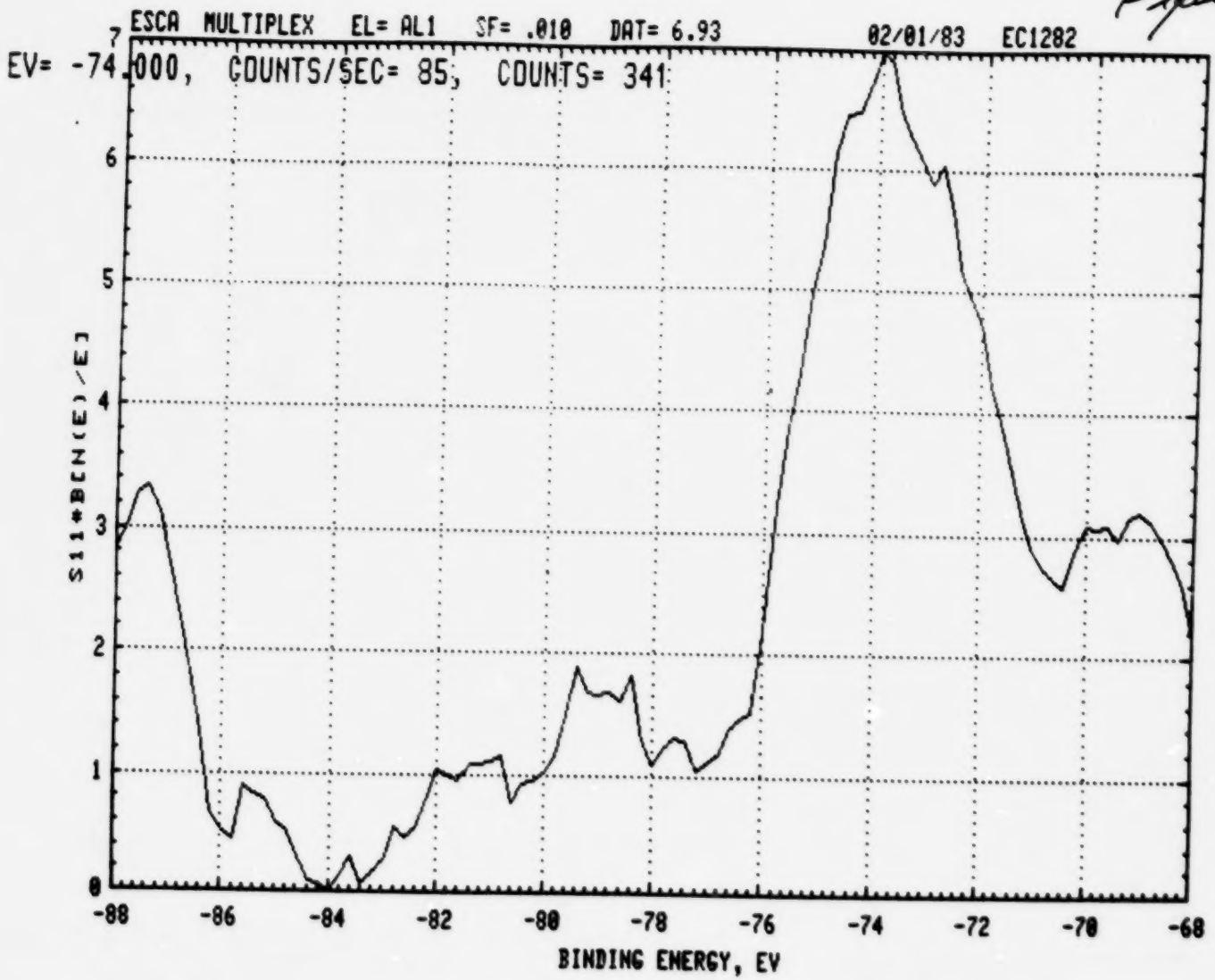

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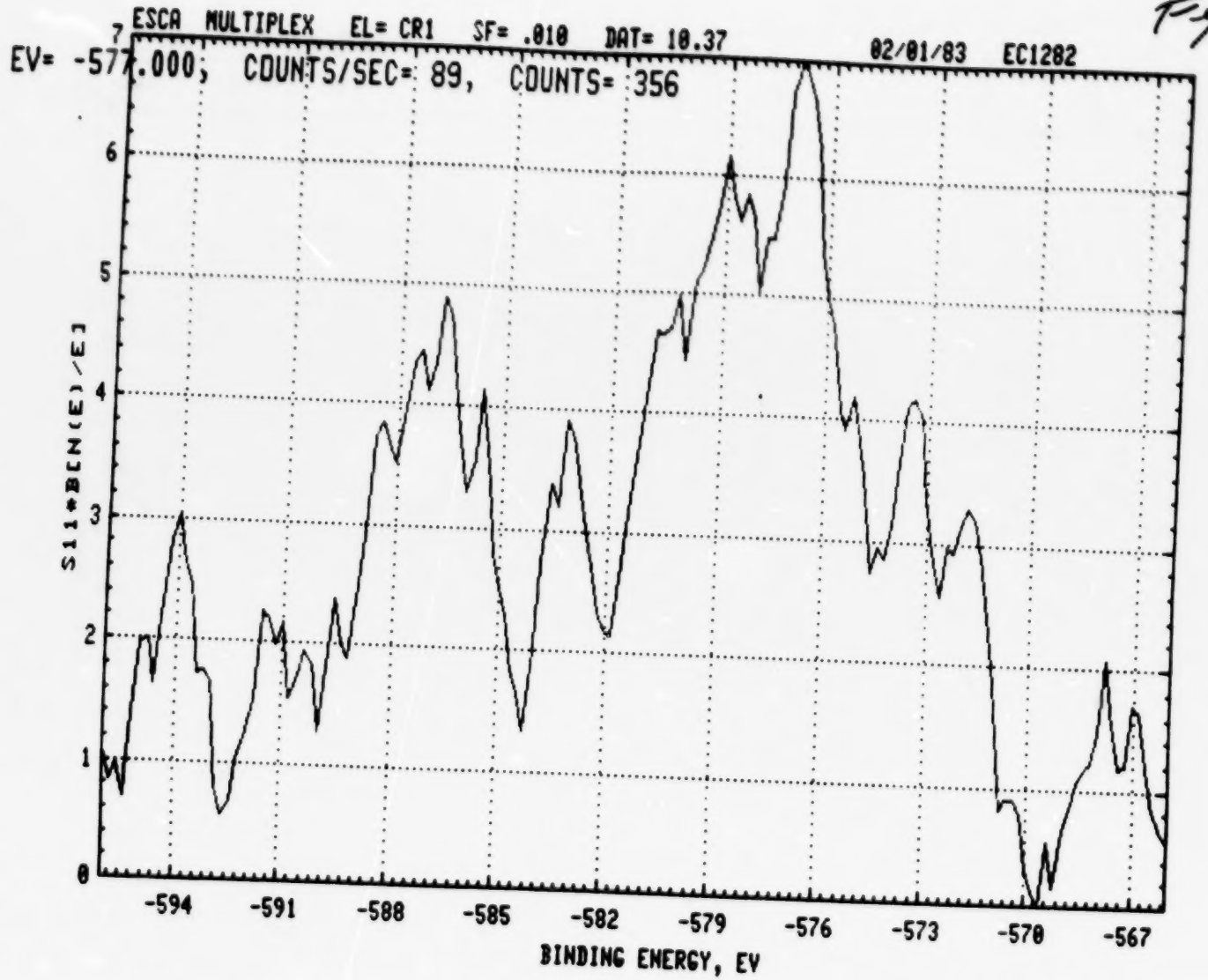

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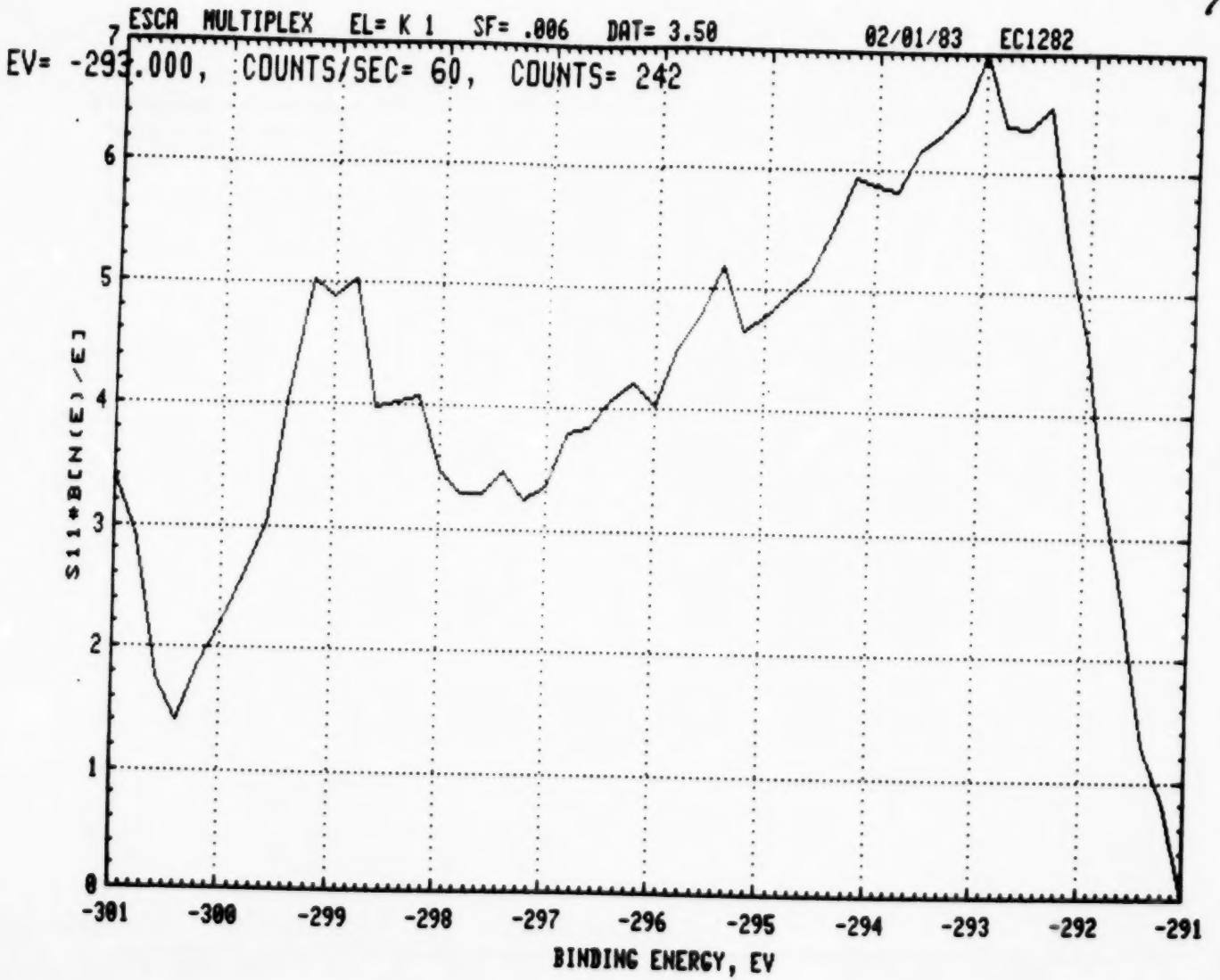

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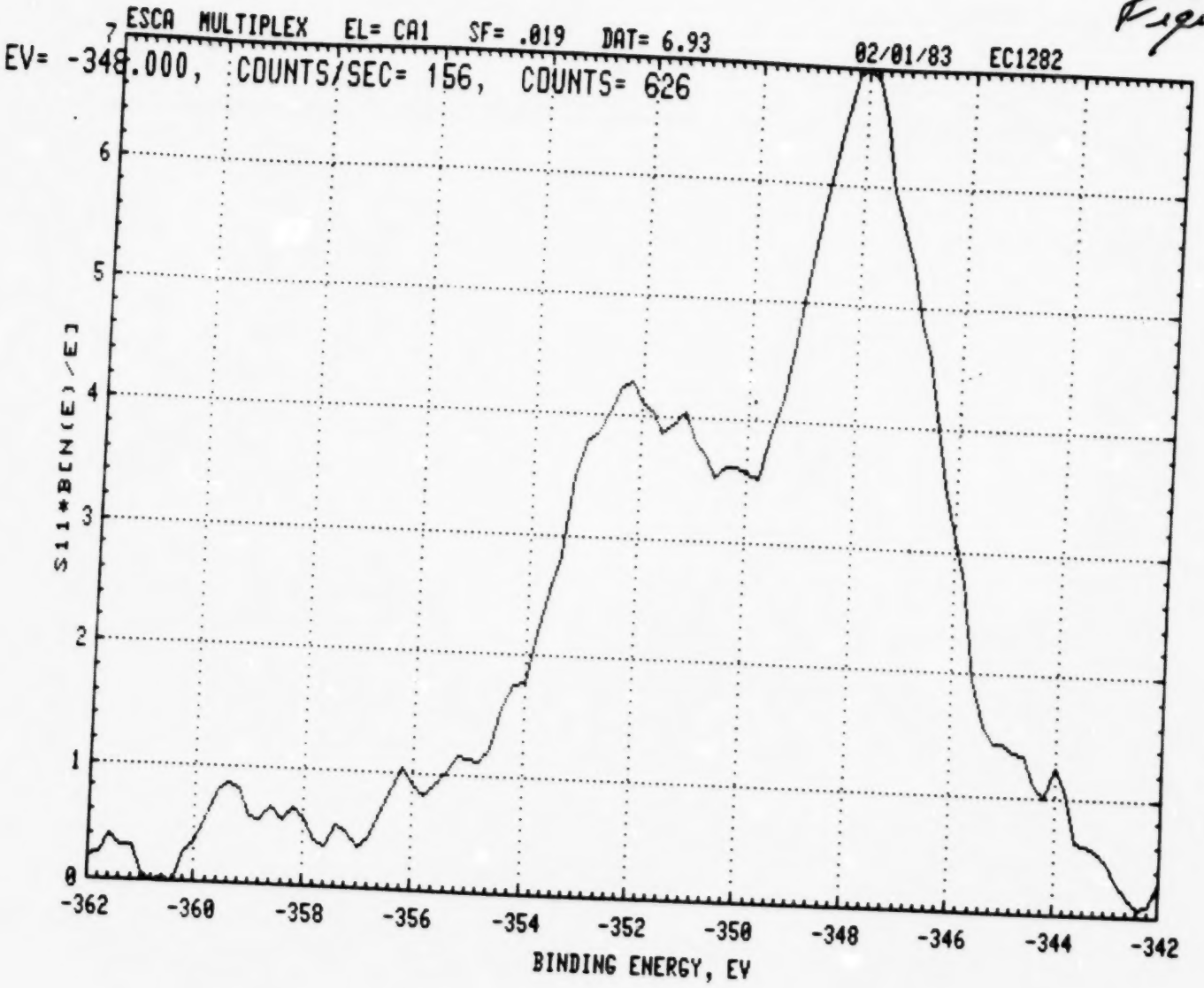

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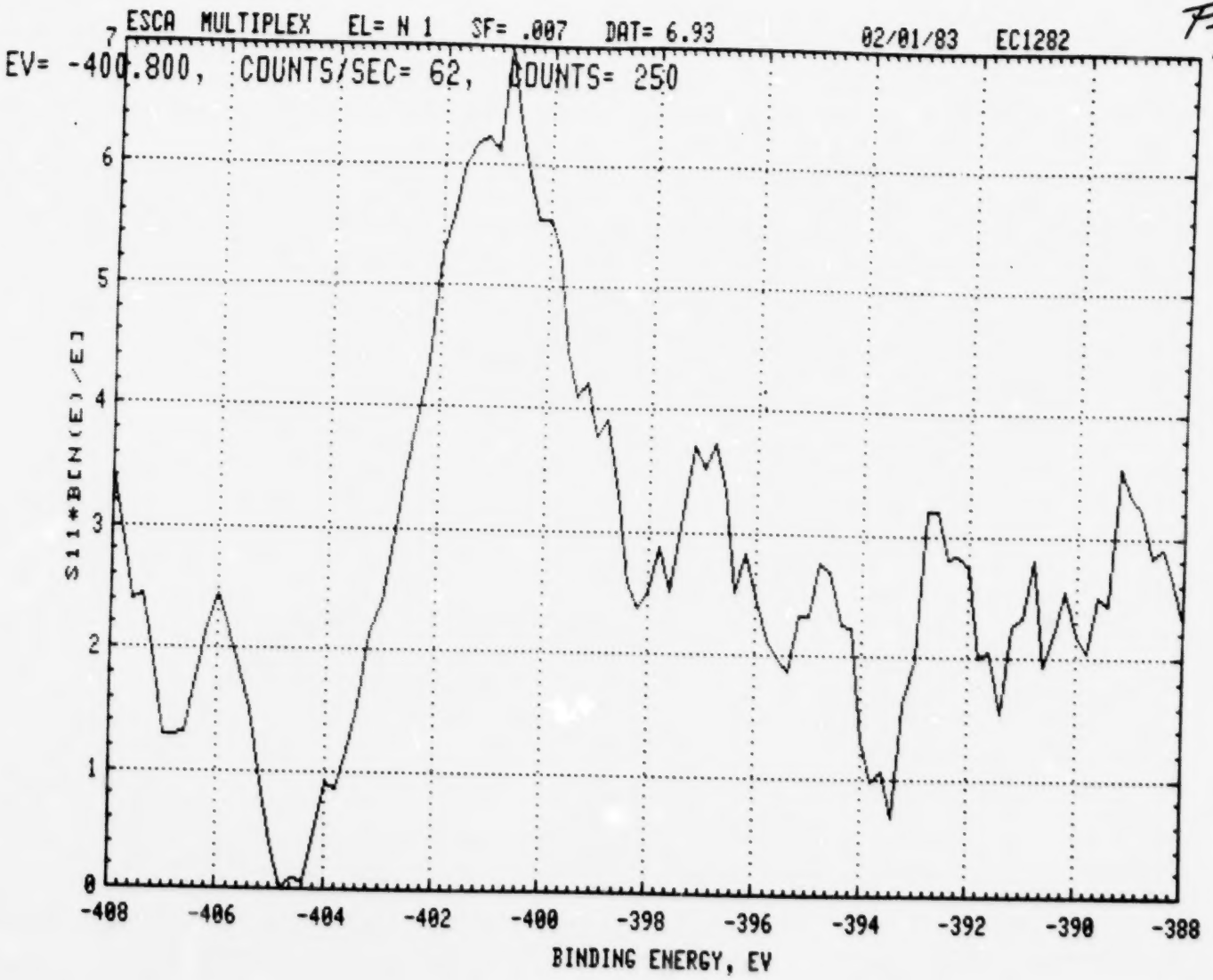

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Figure #12

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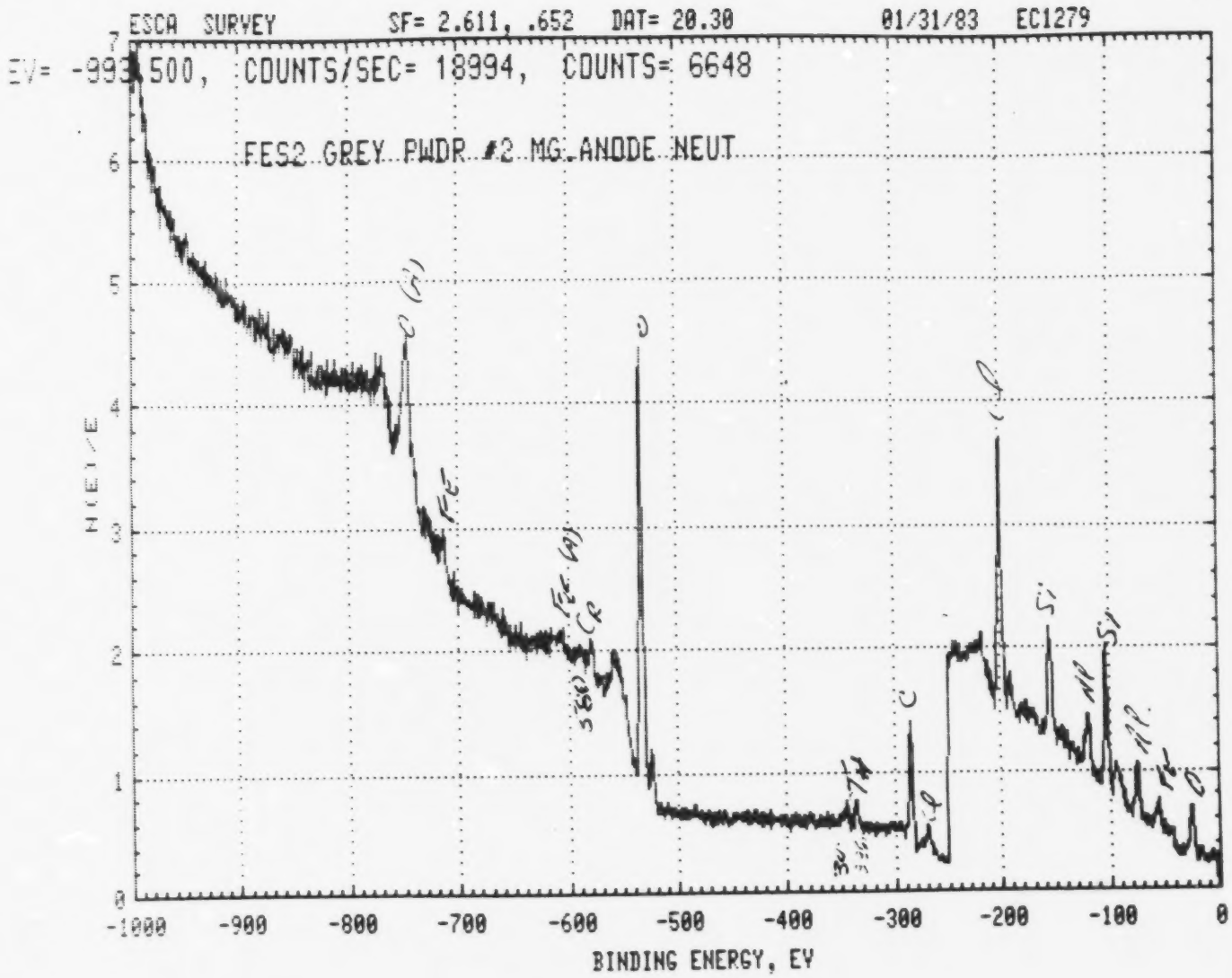

Figure #13

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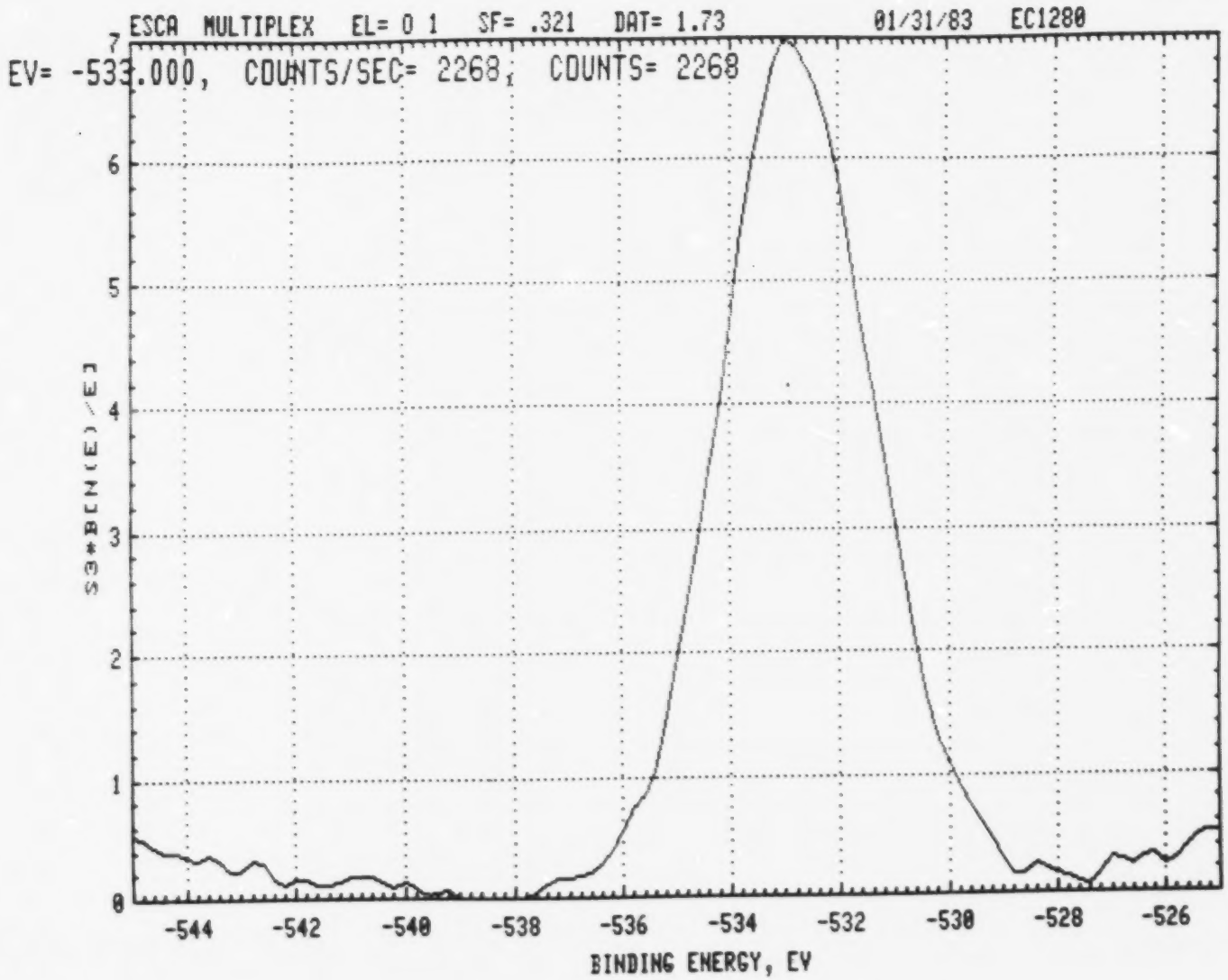

Figure #14

Run #13

Figure #15

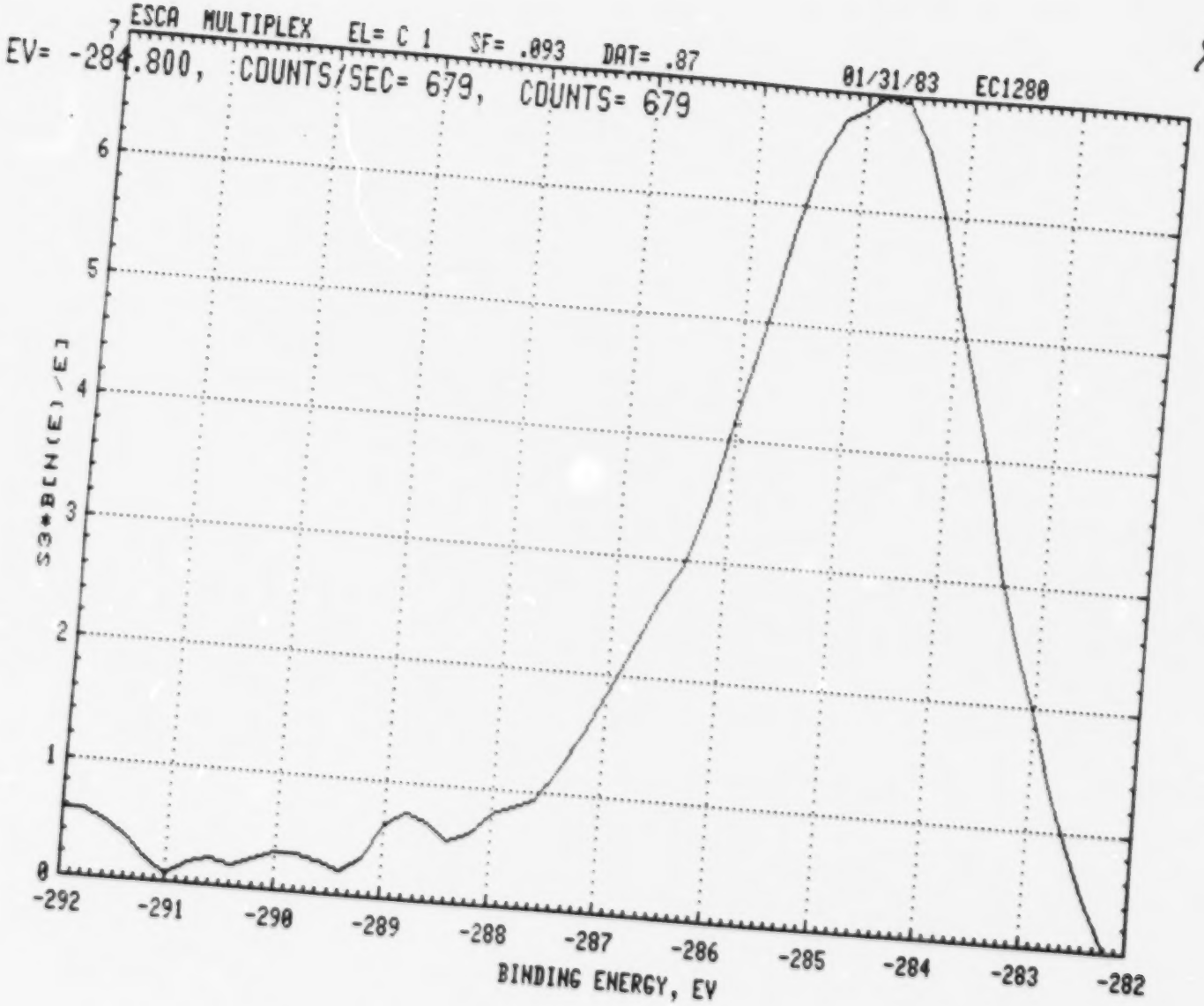

Figure #15

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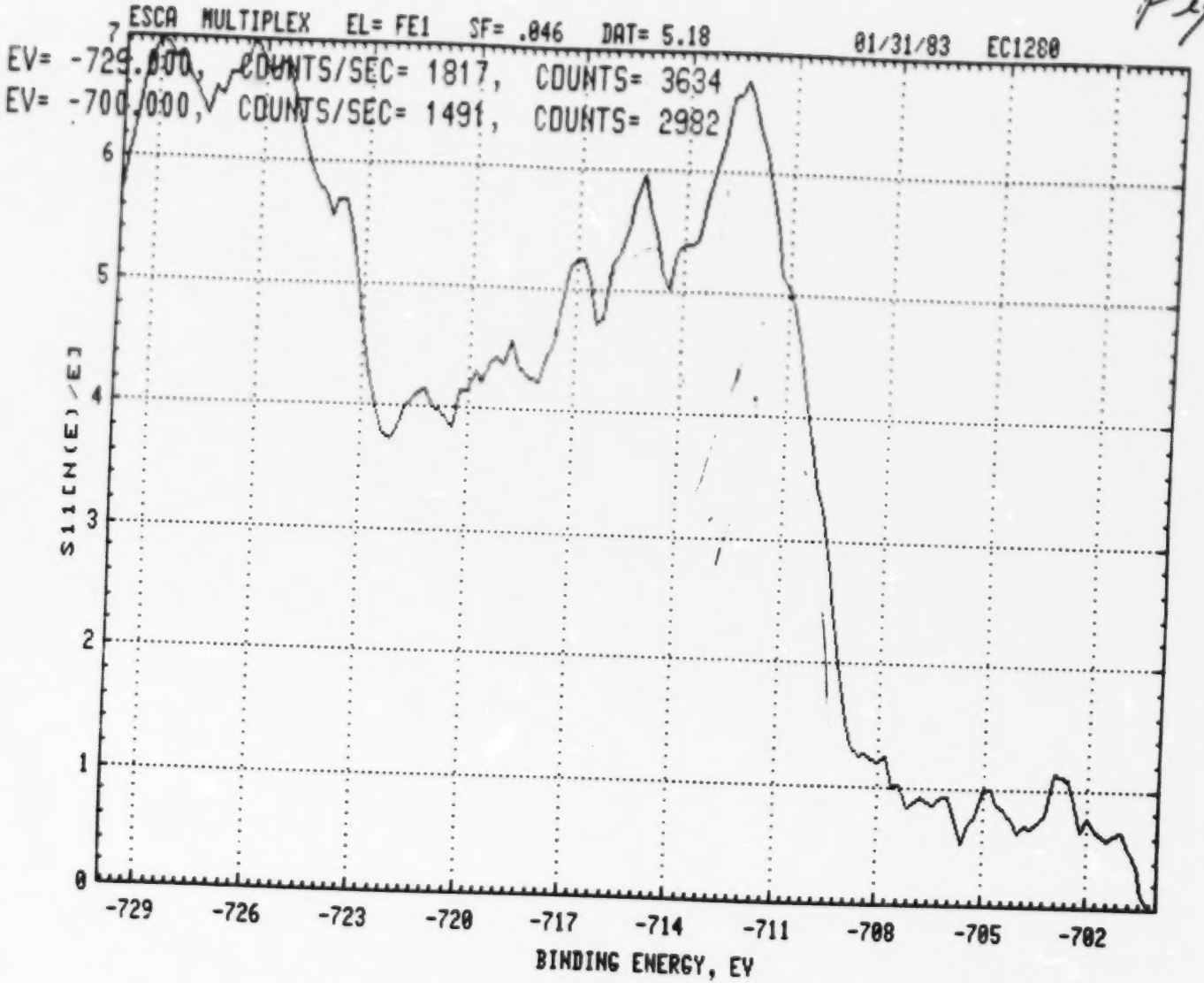

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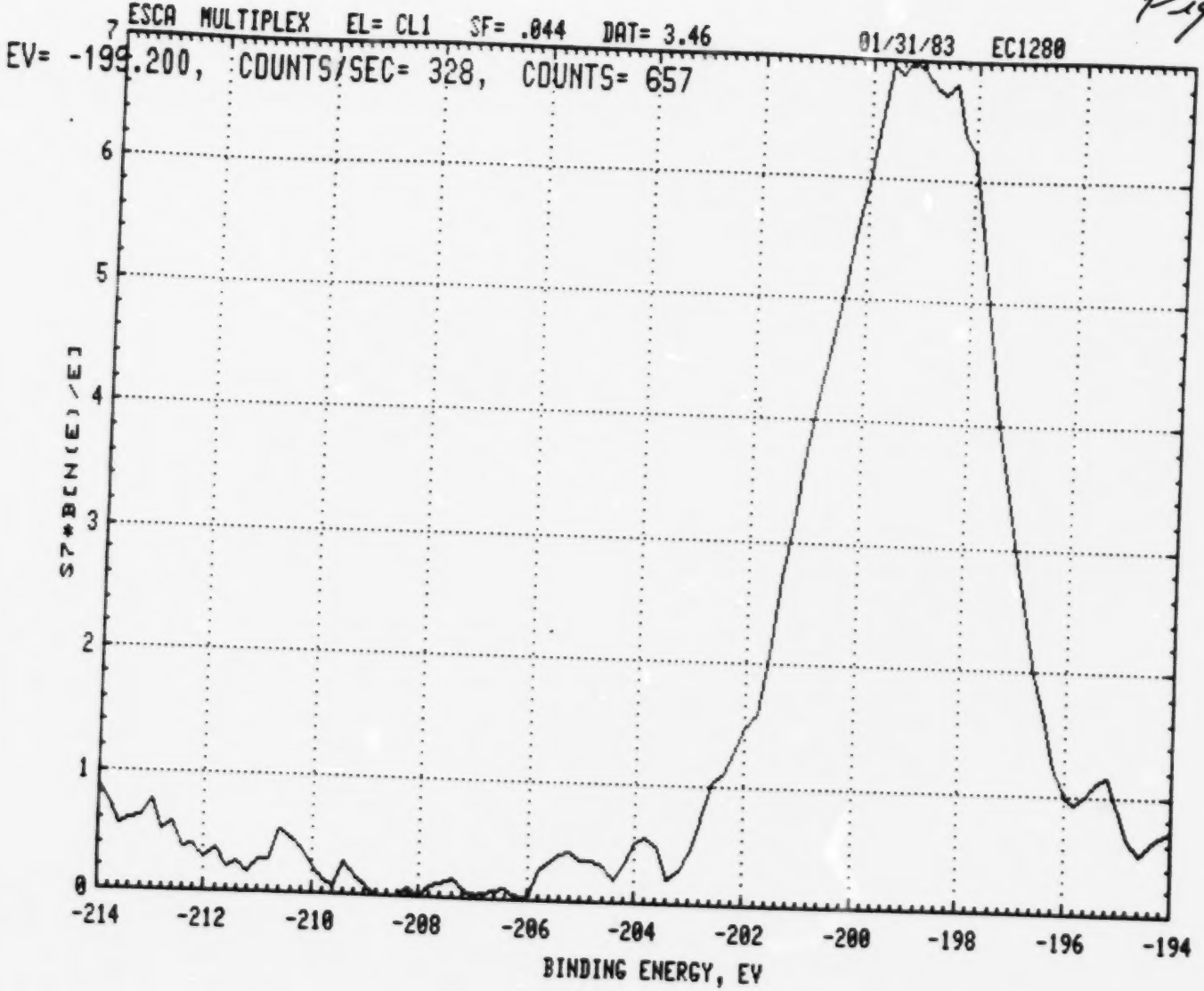

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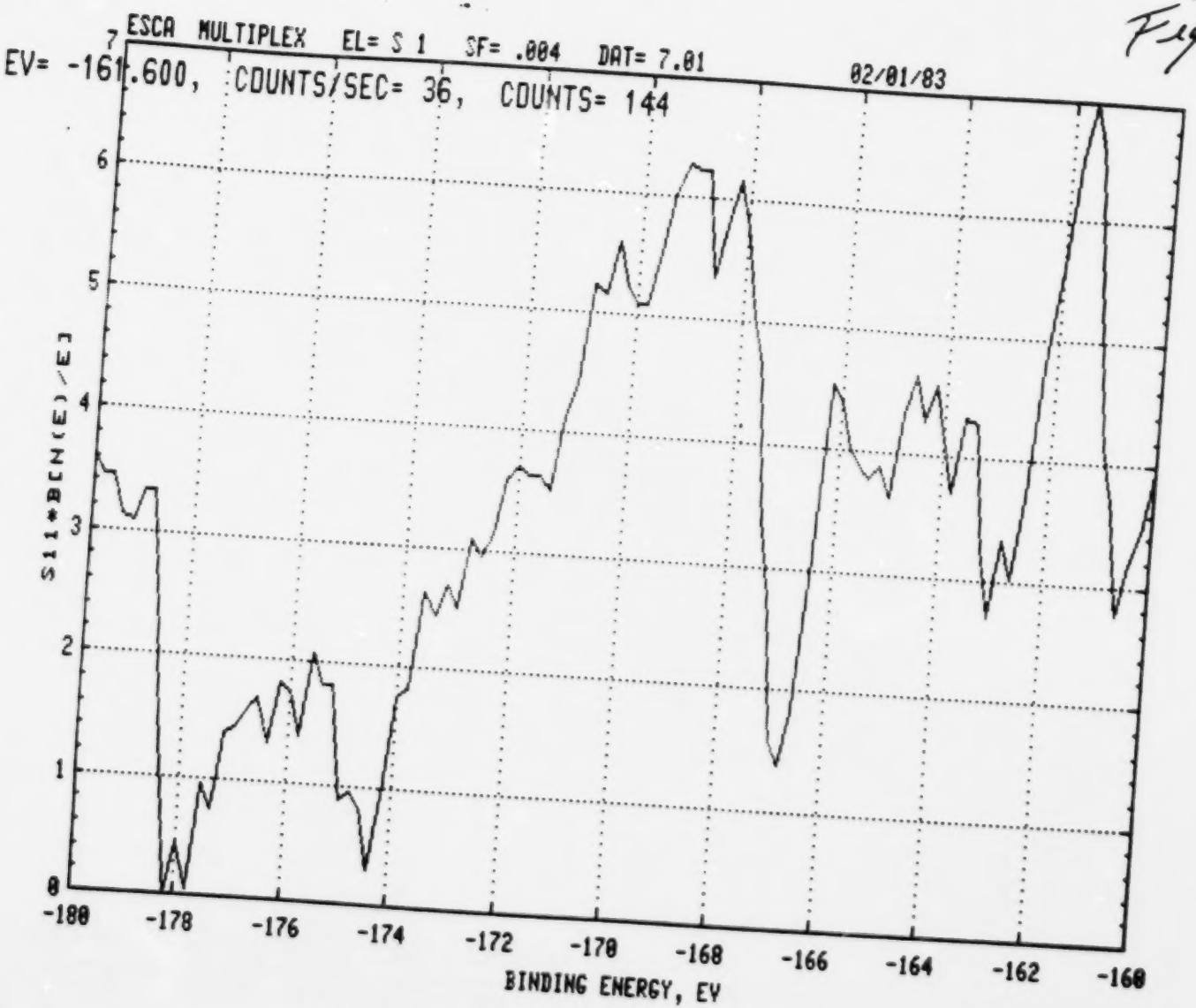

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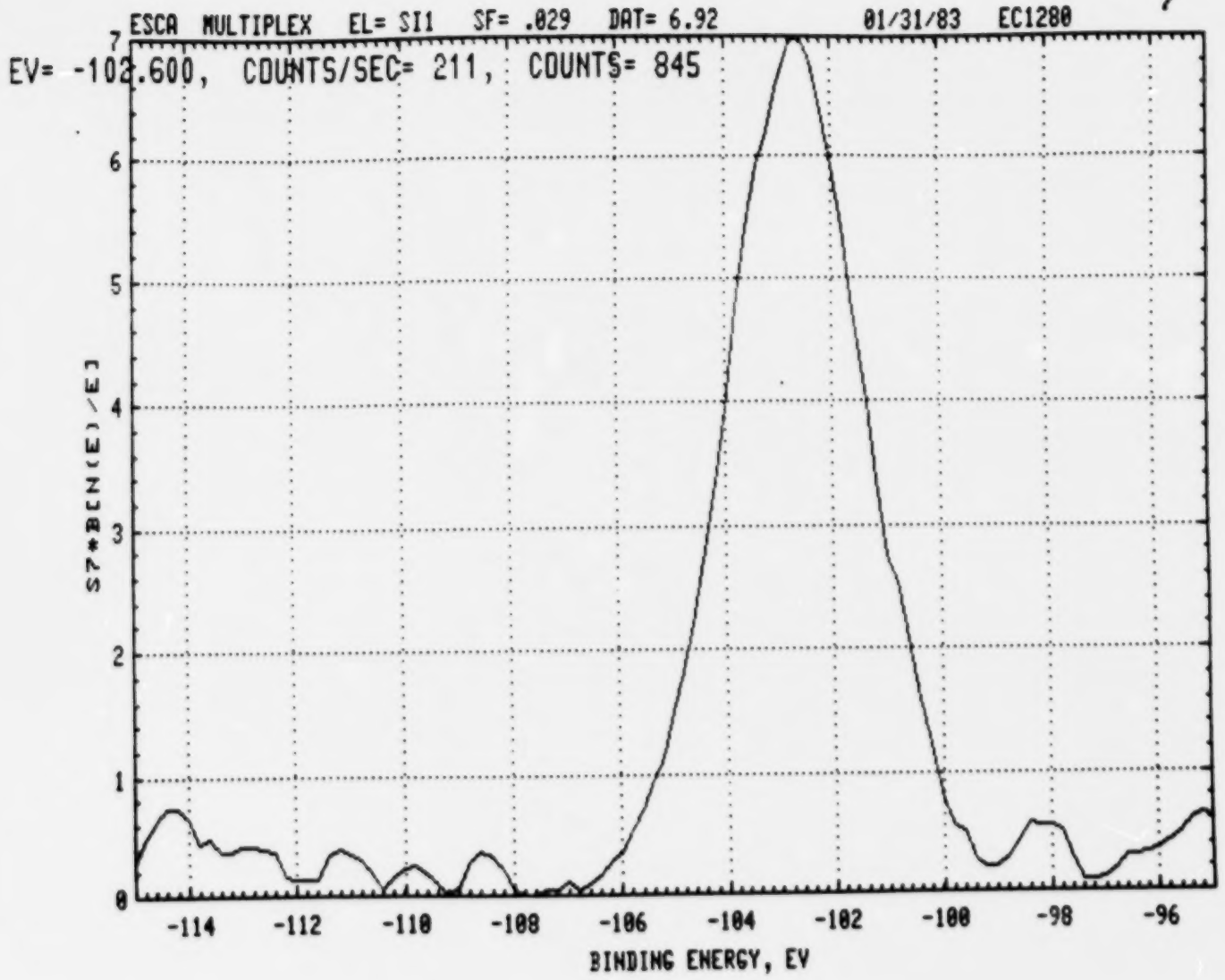

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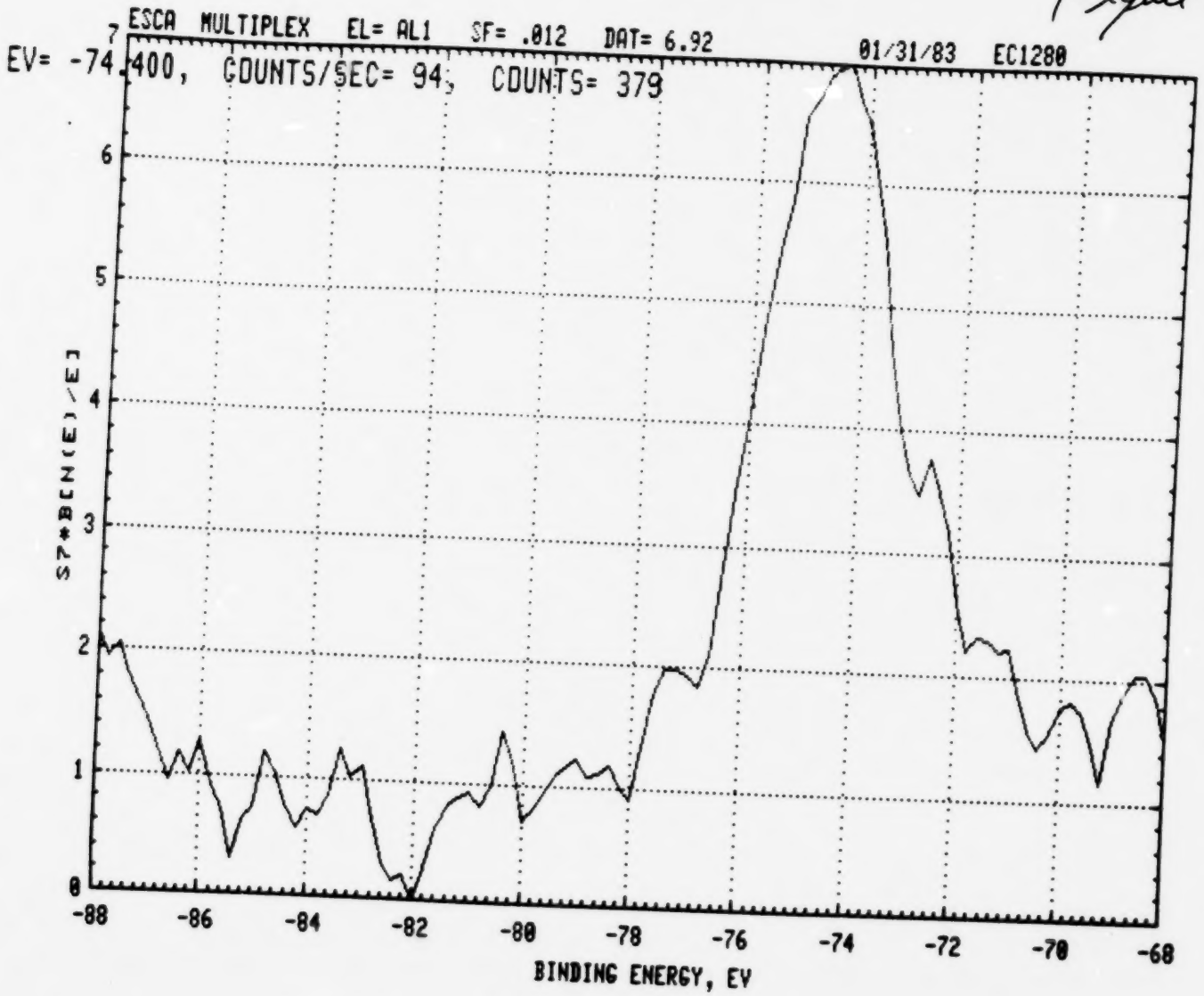

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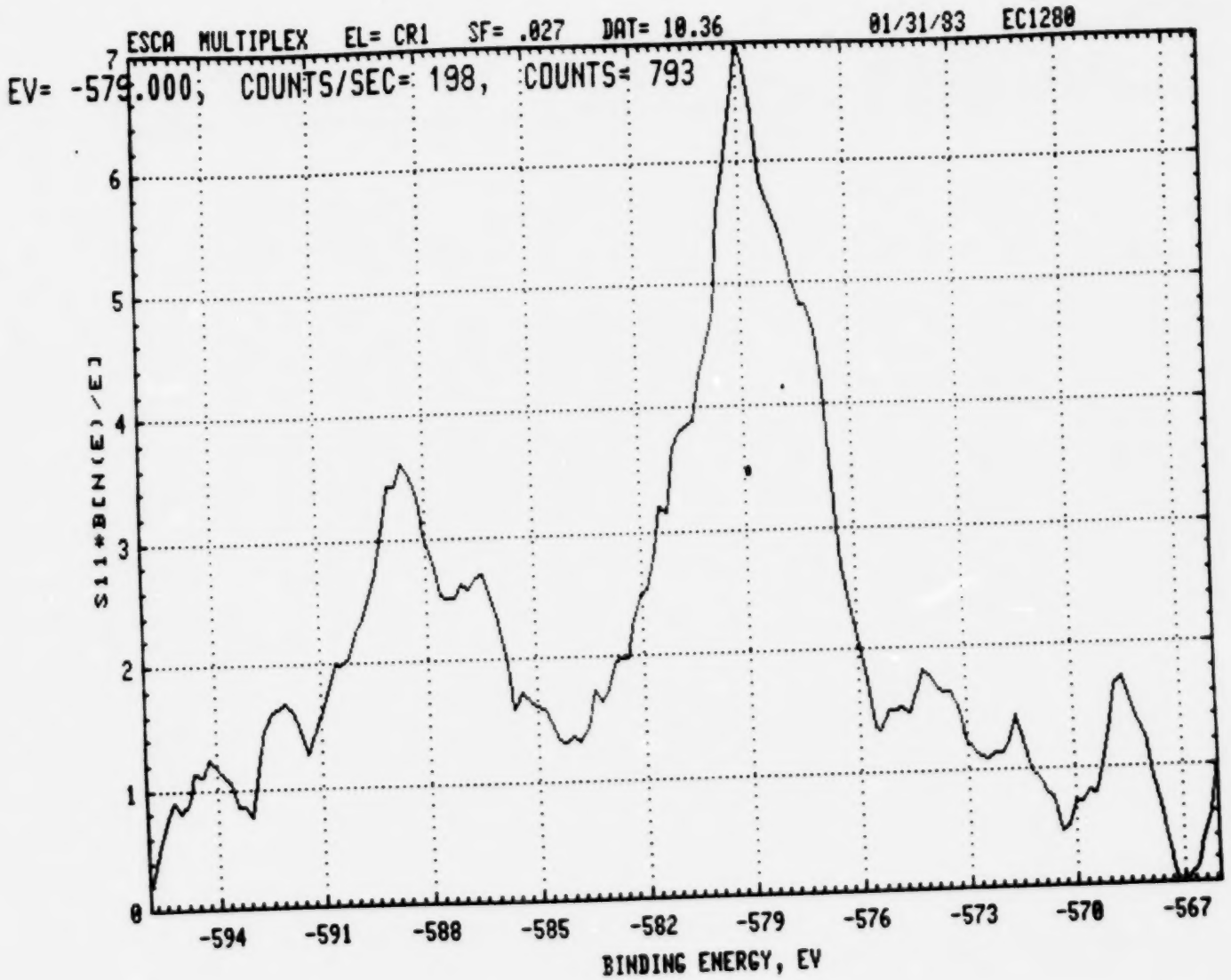

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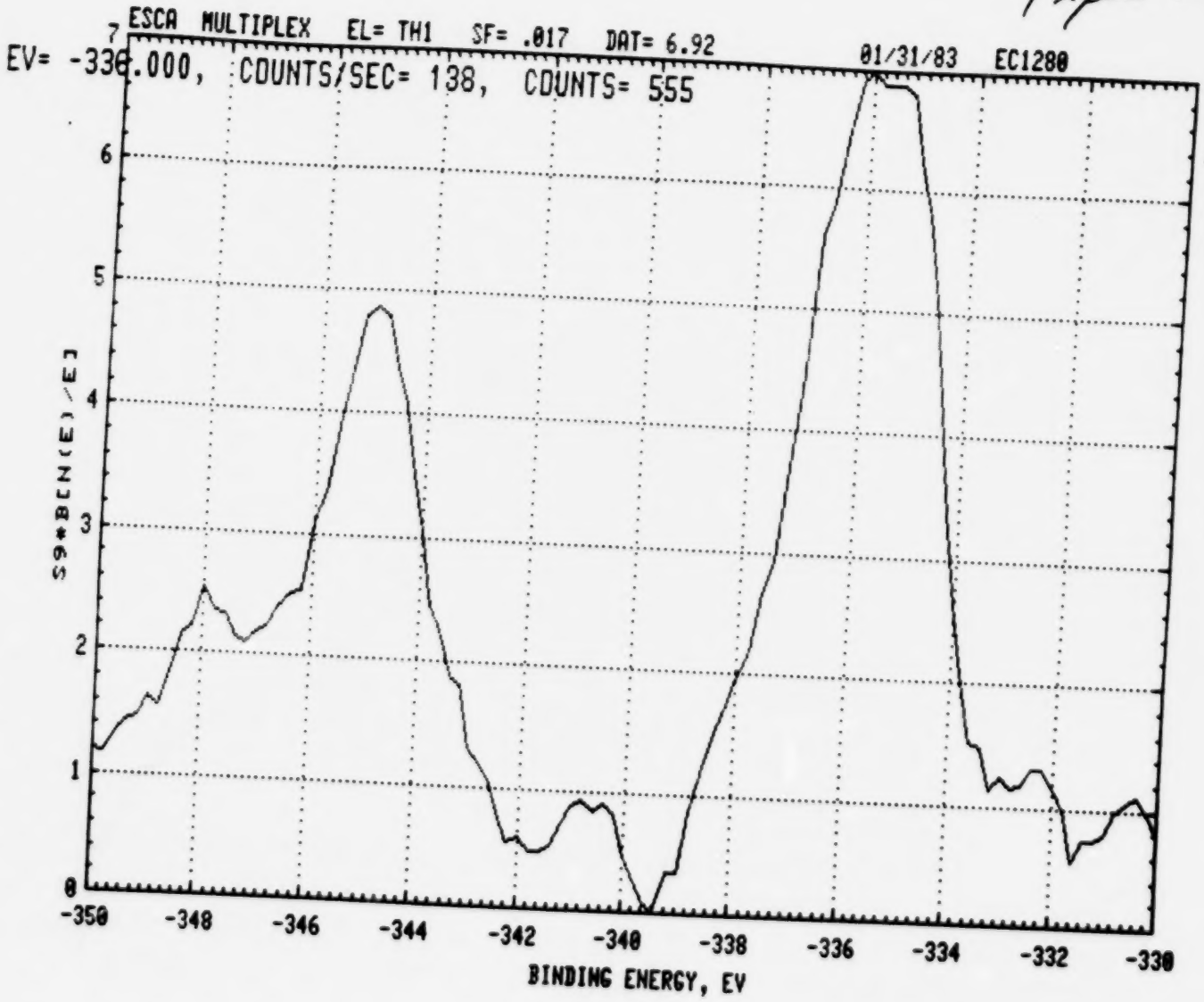
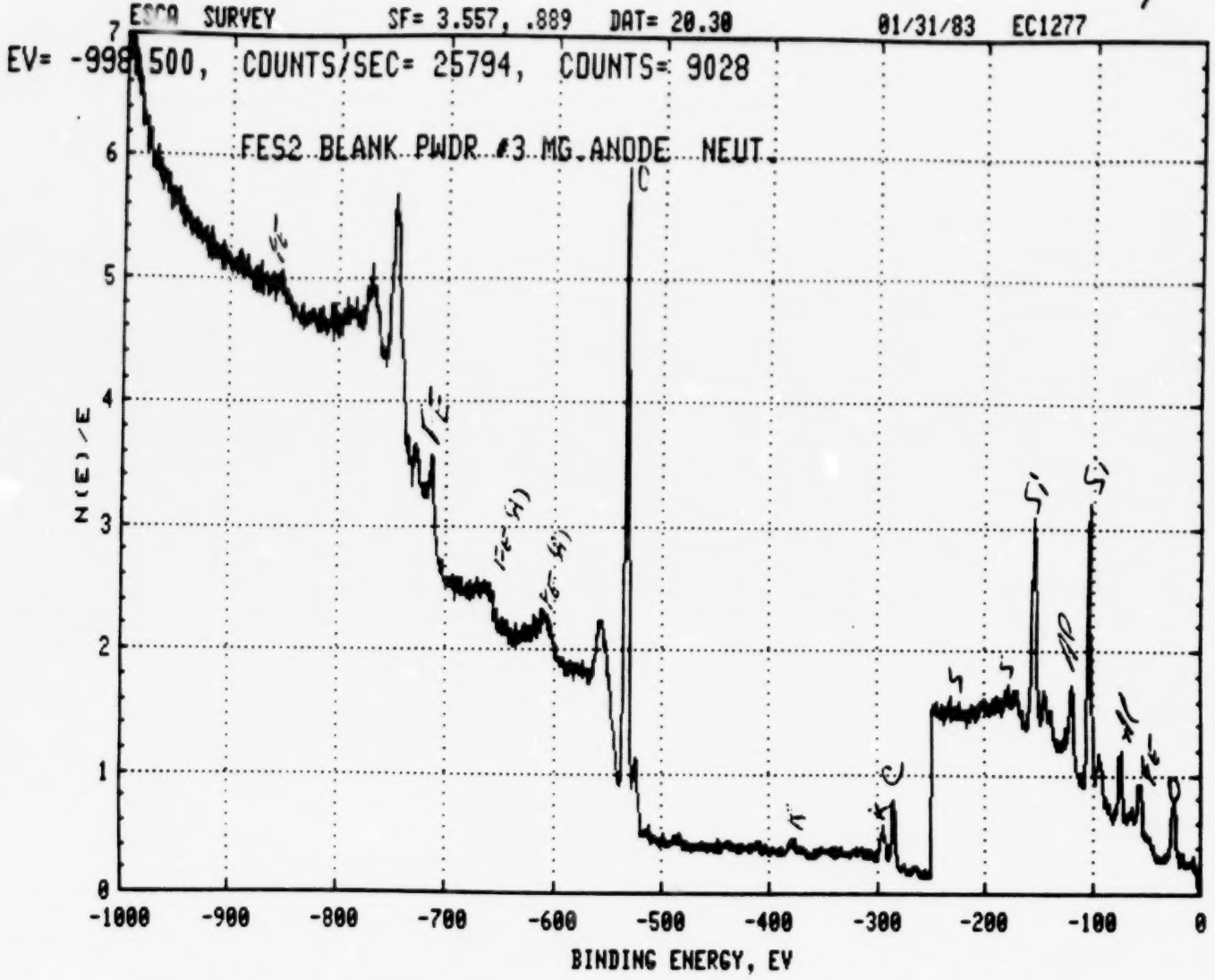


could be
$Th_3(PO_4)_4$
$Th(NO_3)_4 \cdot 5H_2O$

not ThO_2 / $ThCl_4$

Figure #22

Figure #23



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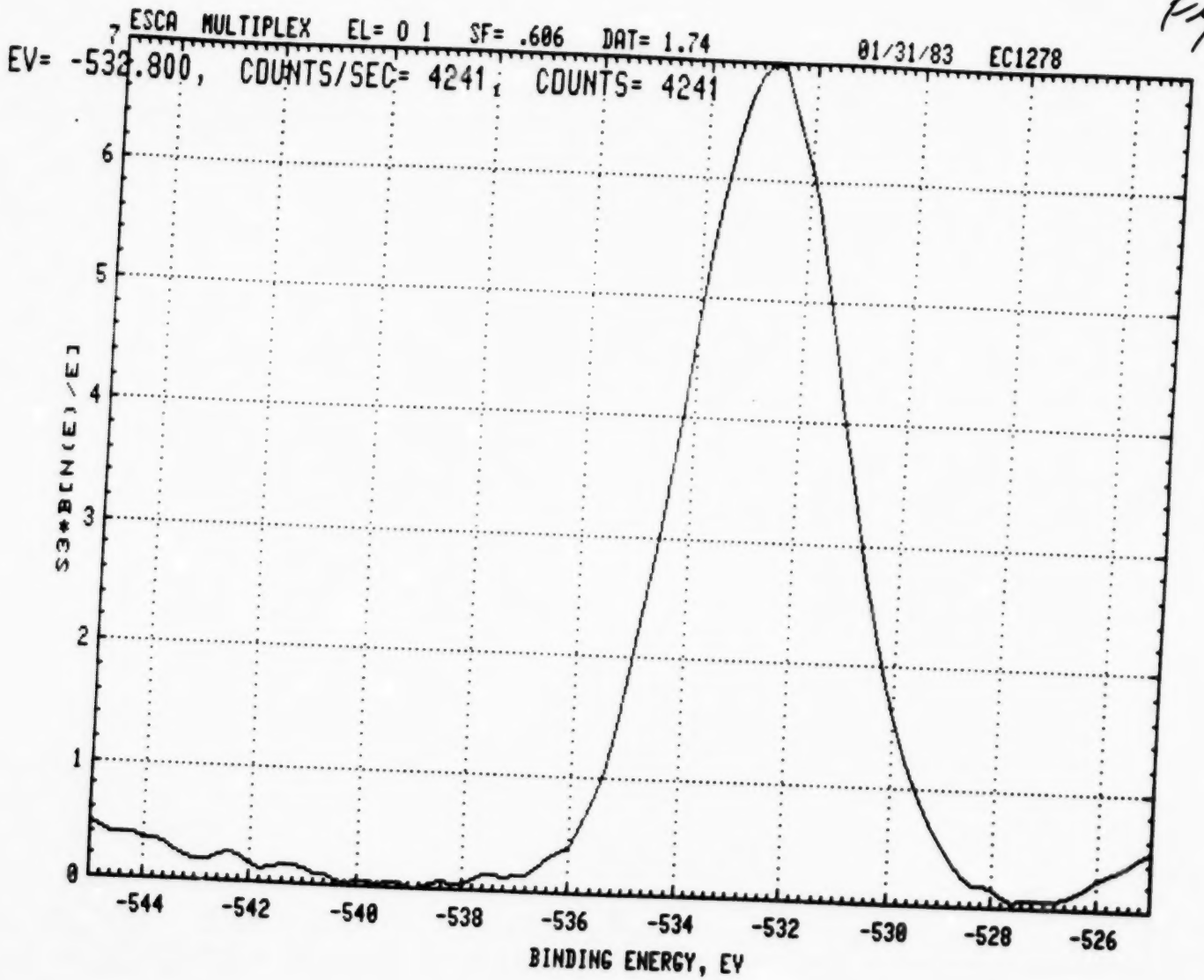

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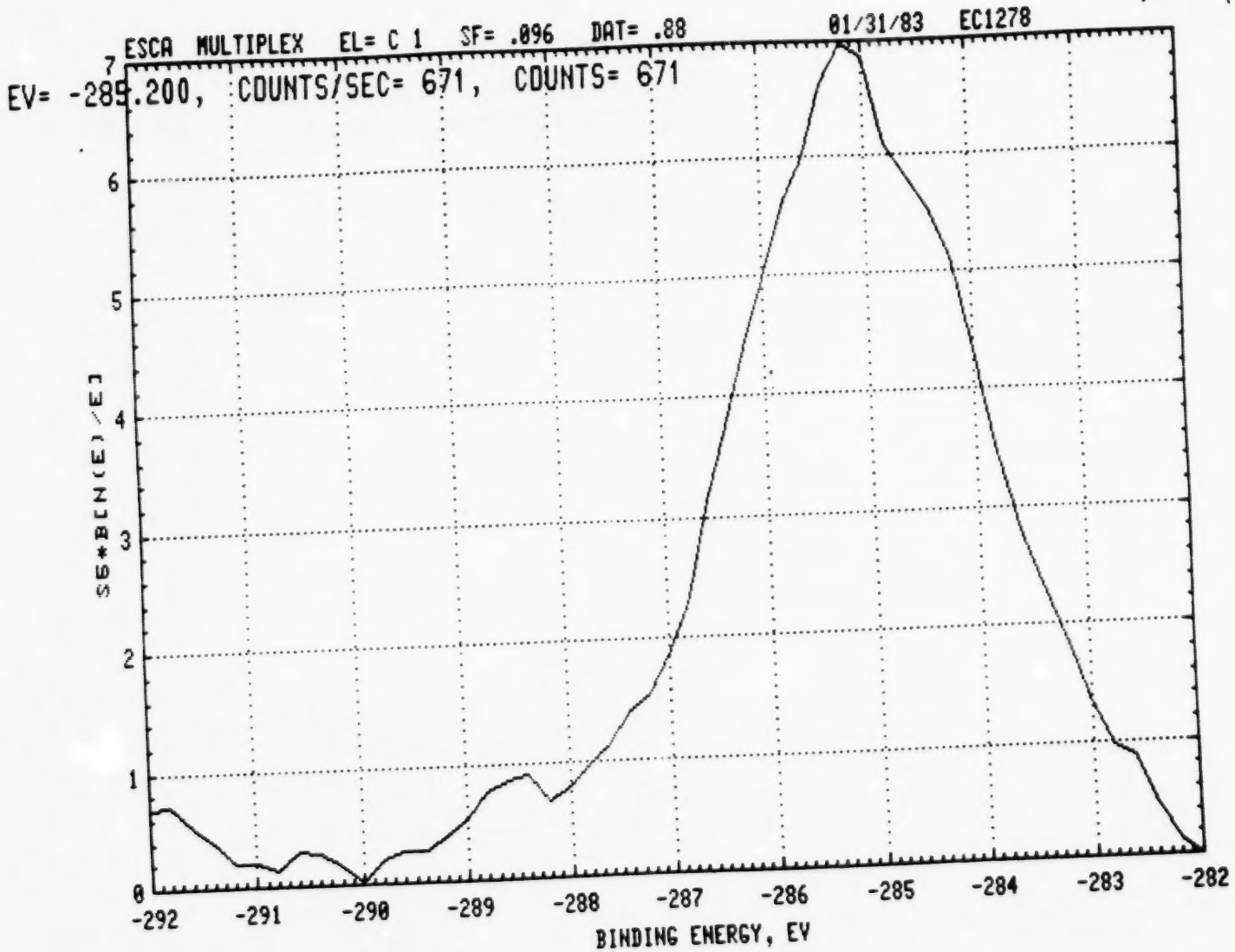

Figure #25

Figure #26

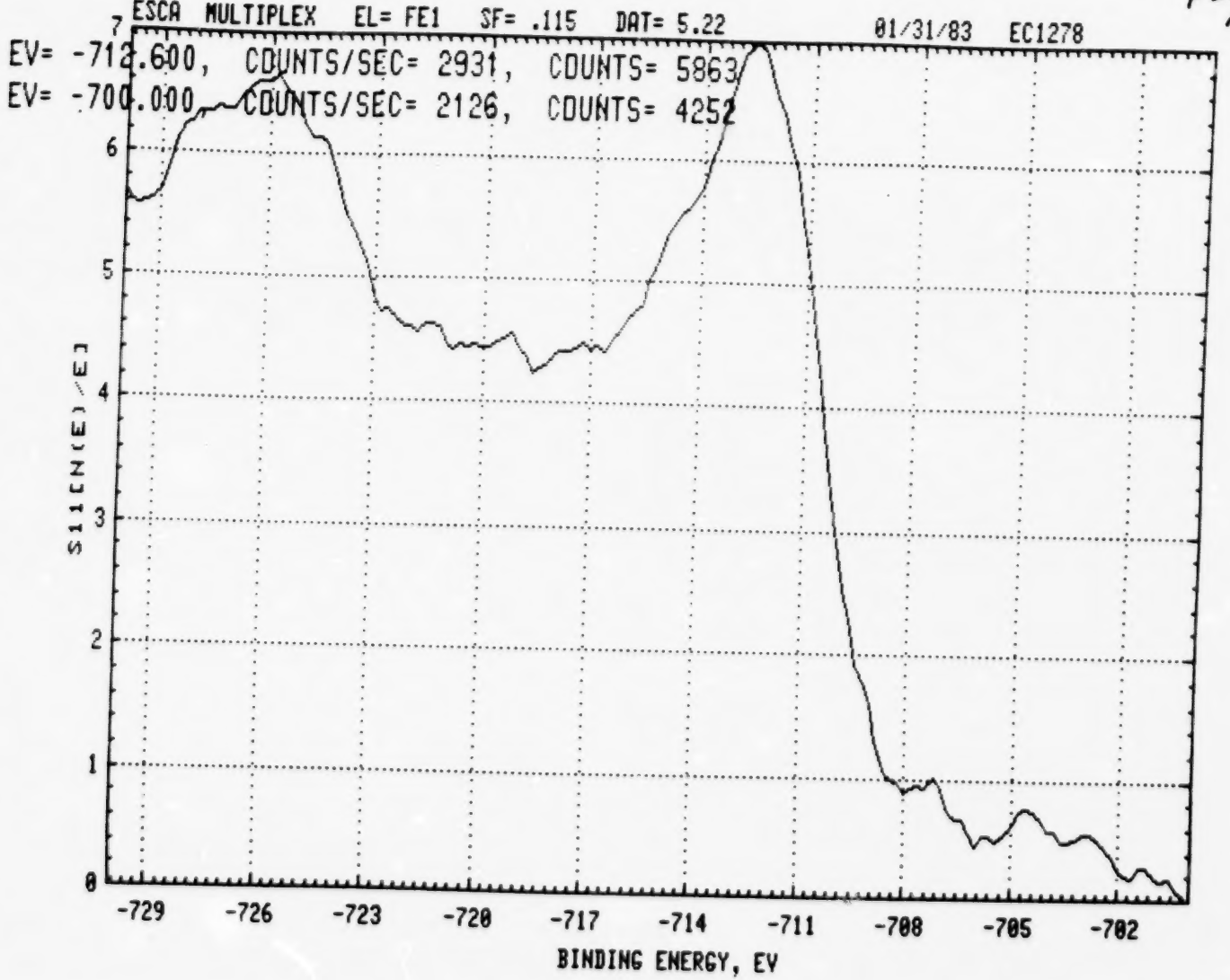

Figure #26

Figure #27

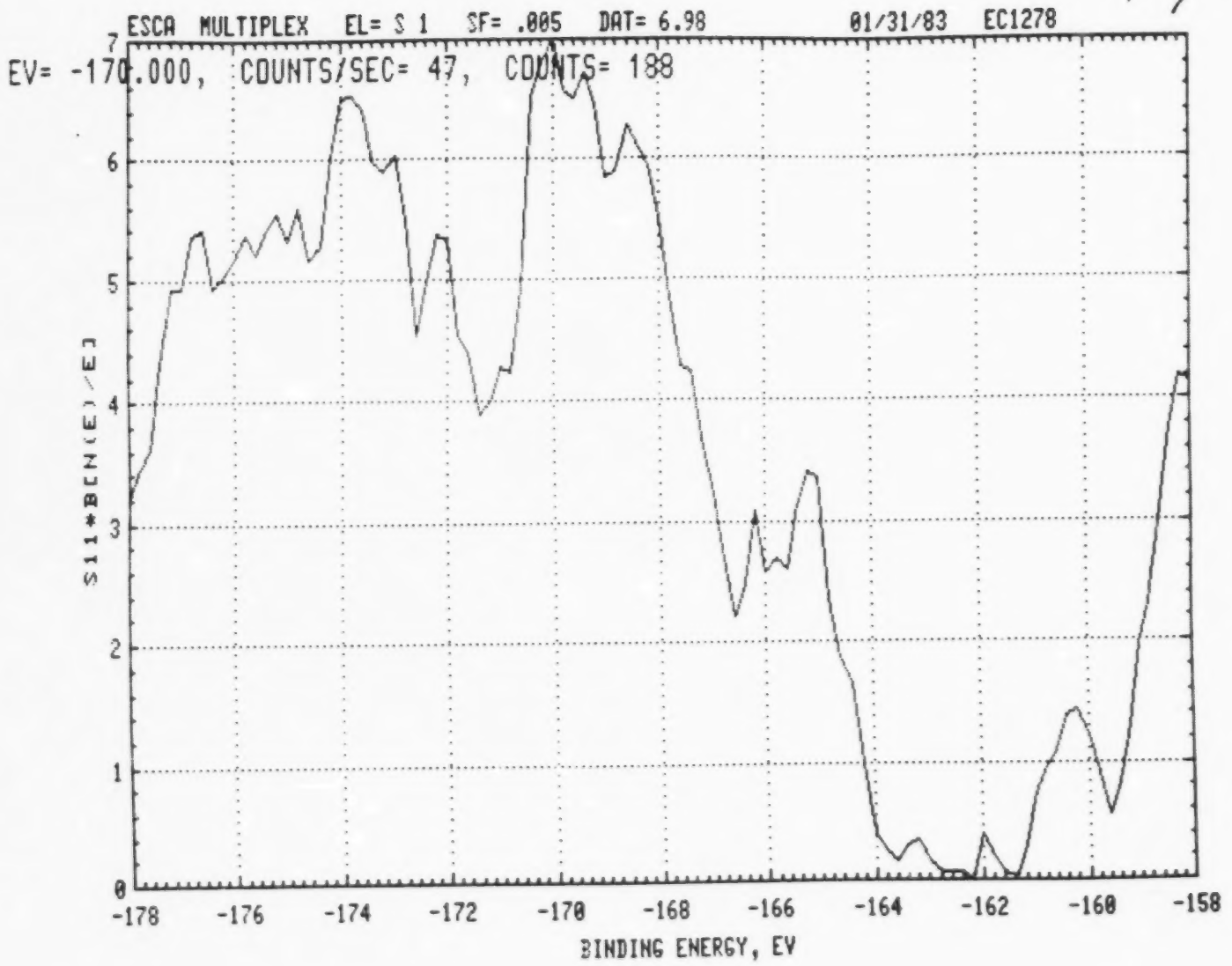

Figure #27

Figure #28

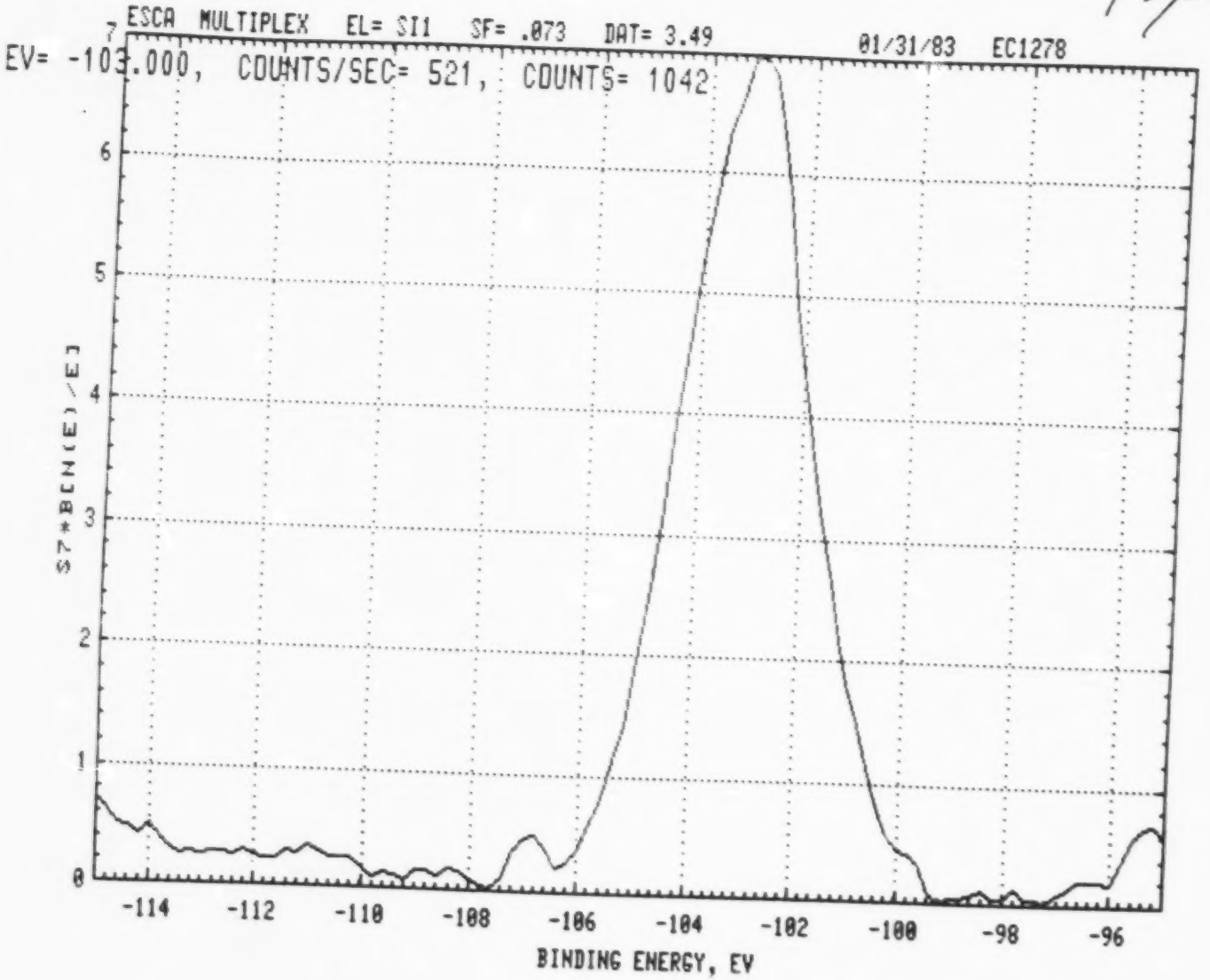

Figure #28

Figure #29

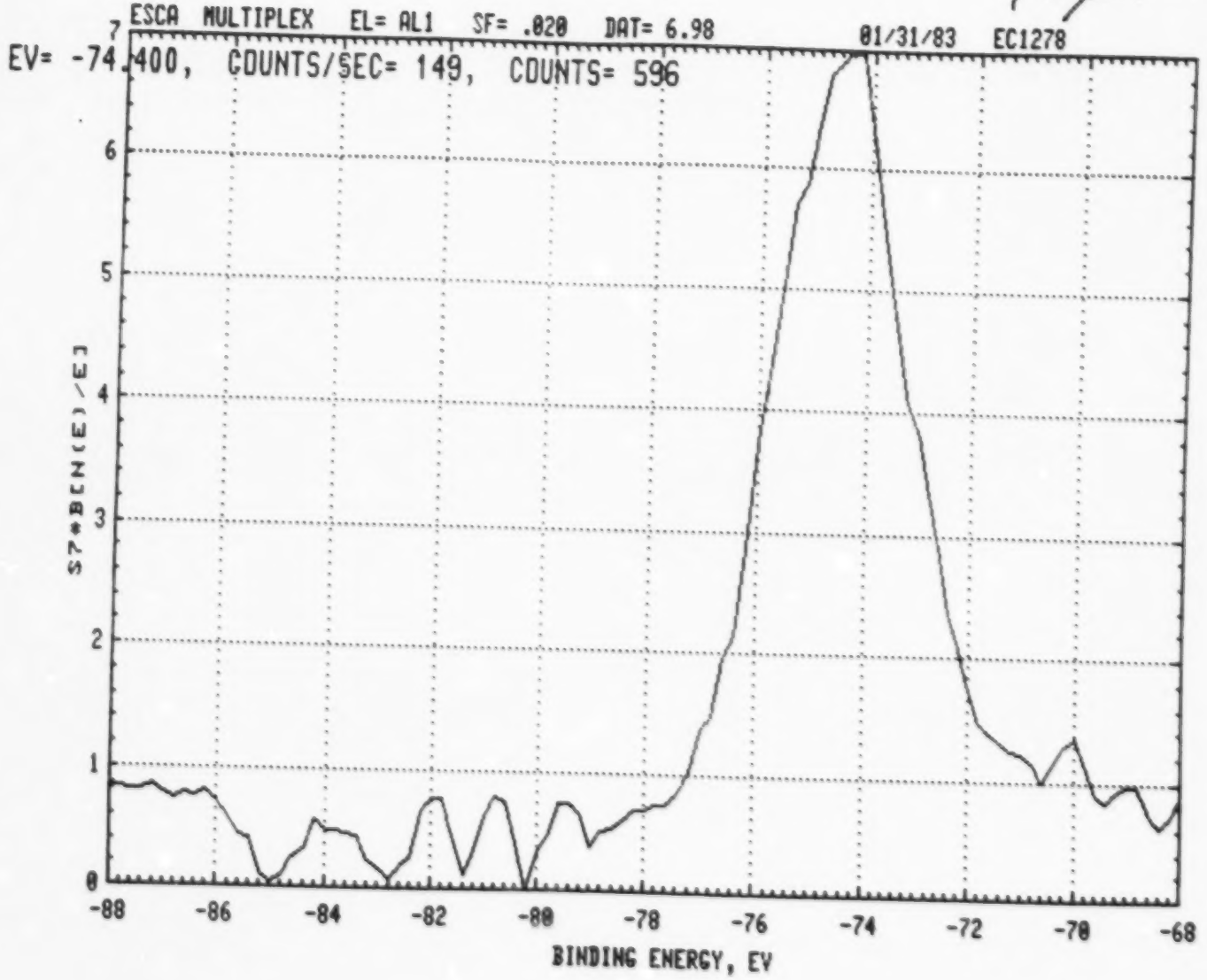

Figure #29

Figure #30

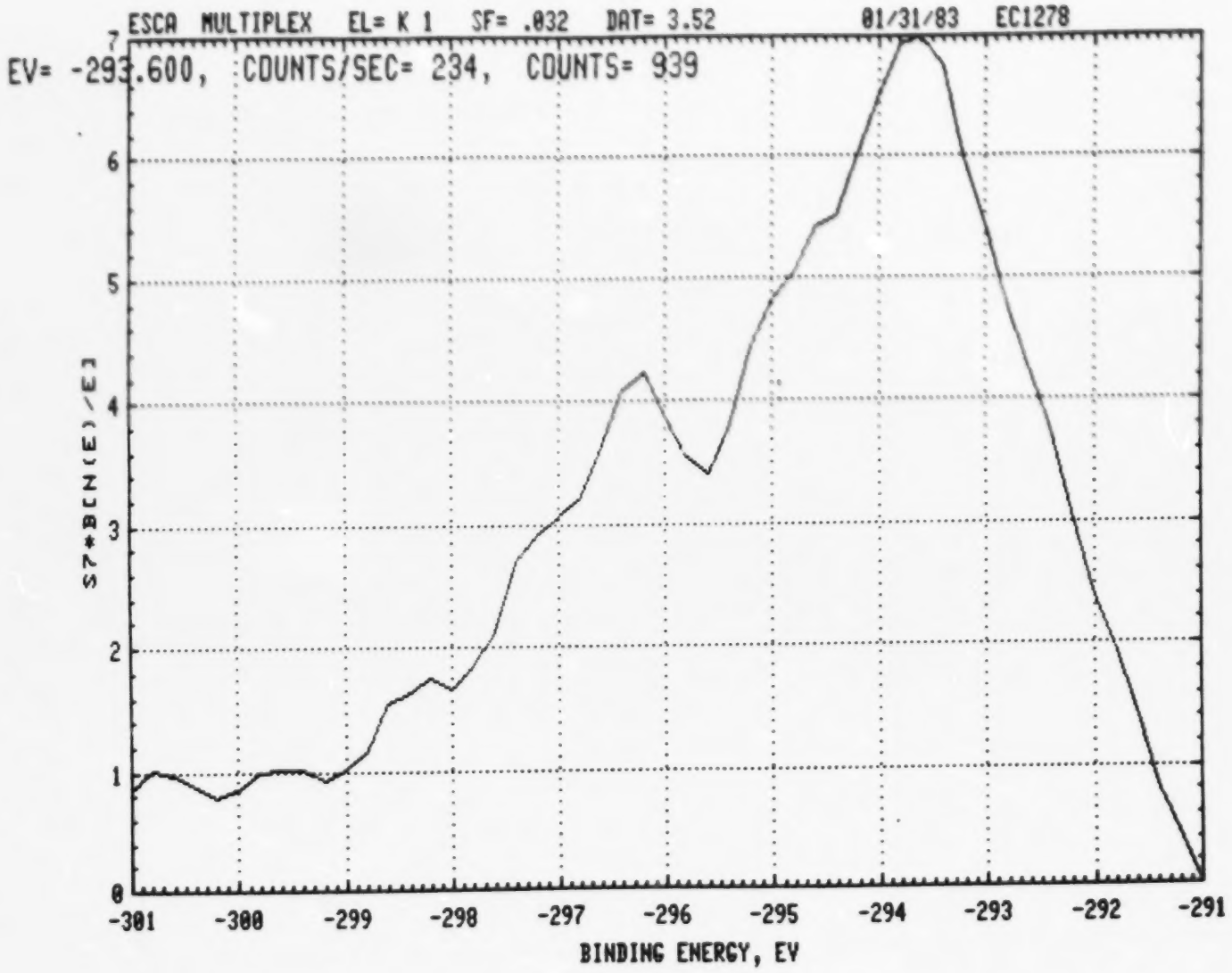

Figure #30

Figure #31

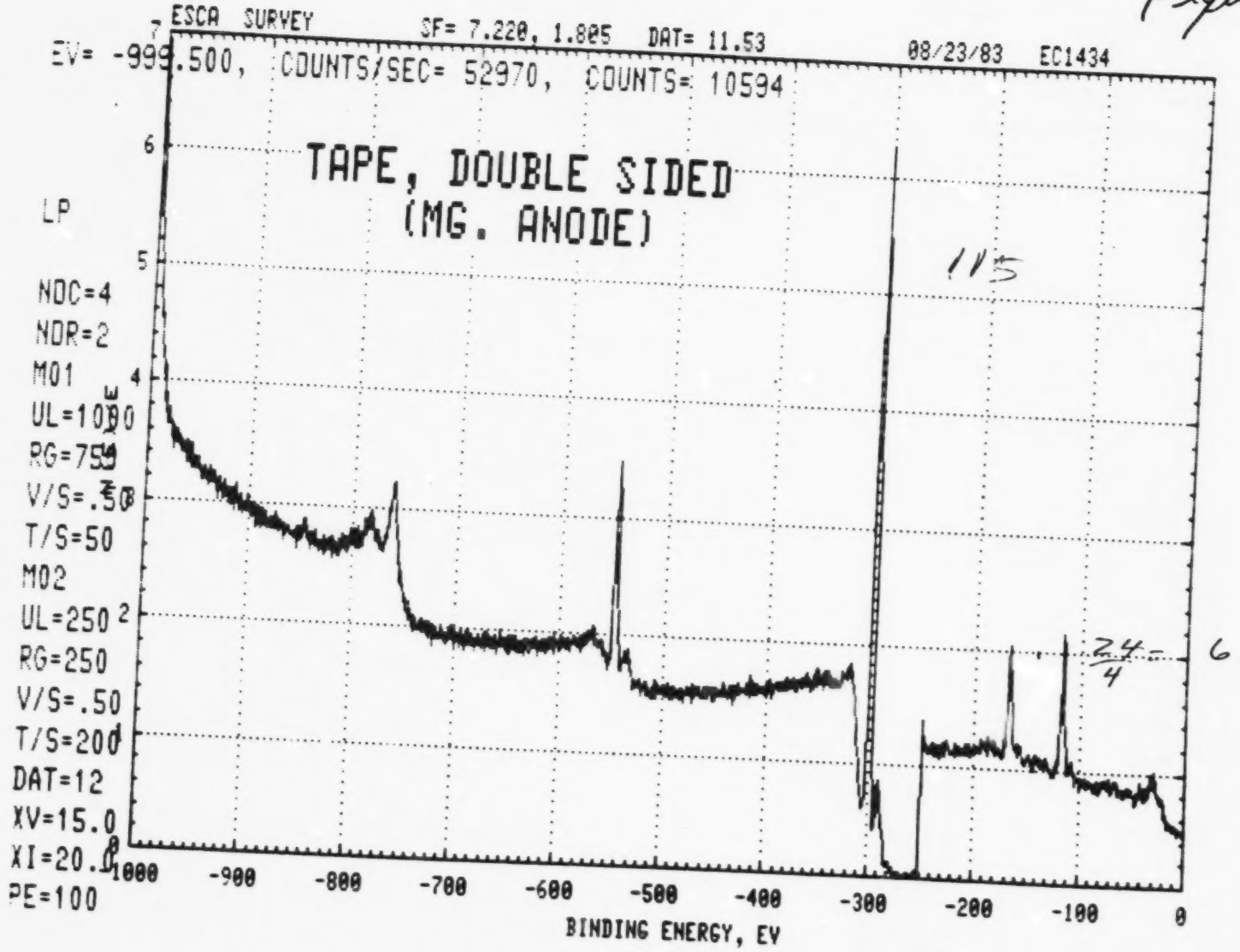

Figure #31

POOR

QUALITY

ORIGINAL